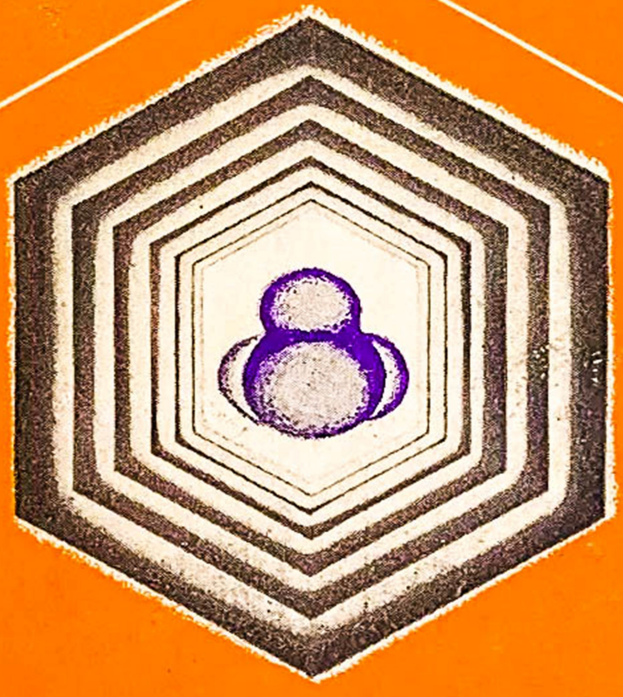
ORGANIC CHEMISTRY

V. M. Potapov and S. N. Tatarinchik



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ORGANIC CHEMISTRY

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PREFACE

Organic chemistry is rapidly developing today. Whole classes of new substances, unusual by their structure and properties, are being discovered, new compounds for diverse applications are being created, modern methods of investigation based on achievements in physics are being used on an ever wider scale, and theoretical conceptions are being elaborated. All this gives rise to certain difficulties in studying organic chemistry, because enormous material must be confined to the framework of a curriculum and of textbooks. The authors are convinced that there is only one way of overcoming these difficulties, and that is to give maximum attention to general principles while inevitably reducing purely descriptive material.

Like a century ago, organic chemistry is based on A. M. Butlerov's theory of the chemical structure of organic compounds. The theory is now supplemented by a better understanding of the nature of the chemical bond and the causes of reactions. Besides Butlerov's classification by the structure of molecules, there is another classification, i.e., that by the type of reactions. It is precisely owing to the revelation of the nature of organic reactions that the transformation of organic substances could be regarded not as a set of diverse exceptional cases which are difficult to remember, but as a streamlined system.

The authors sought to expound the general principles of organic chemistry within the framework of this textbook, regarding the study of the theory not as an aim in itself, but as a means of understanding and remembering the material better and ultimately of facilitating its assimilation. But organic chemistry cannot be studied without knowing the techniques of obtaining specific substances, their properties and fields of application. The authors endeavoured above all to tell about the practically important organic substances used in industry, agriculture and medicine.

This book is based on the classification of organic compounds by functional groups, which determine the chemical behaviour of organic substances. At first, the authors consider various types of hydrocarbons that constitute a single large family which is bound together by numerous mutual transformations, and then all the halogen derivatives, hydroxyl derivatives, and so forth.

The authors will be grateful to readers for their suggestions and remar s that may help to improve the book further.

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INTRODUCTION

I.1. Subject of Organic Chemistry and Its Practical Importance. Organic chemistry is usually defined as the *chemistry of carbon-containing compounds.* Such a definition immediately begs the question: how about such well-known inorganic substances as carbonic and hydrocyanic acids and their salts, since they also contain carbon? Indeed, it is impossible to draw ana bsolutely clear-cut line between organic and inorganic chemistry. However, the bulk of carbon compounds are organic substances.

There is also another definition: *organic chemistry is the chemistry of hydrocarbons and their derivatives.* The profound meaning of this will become clear later. For the time being, it should be explained that hydrocarbons are the simplest organic substances consisting of atoms of only two elements: carbon and hydrogen. Derivatives are substances of greater complexity which can be obtained by substituting hydrogen atoms in hydrocarbons for atoms of other elements or for complex groups.

The name *organic chemistry* originated at the beginning of the nineteenth century, when it was ascertained that carbon-containing substances are the main component of plant and animal organisms.

Originally, the task of organic chemistry was to study substances existing in living nature. However, *products of organic synthesis*, i.e., artificial substances, many of which are not found in nature, gradually began to grow in importance. As for natural substances, simple and eventually more and more complex ones were studied, and then an investigation began to be made of *chemical processes* constituting the basis of vital activity. Modern organic chemistry deals with both natural and synthetic organic substances: their structure, the ways of obtaining them, their properties, and the possibilities of practically using them. In addition, apart from purely chemical methods, i.e., those of analysis and synthesis, diverse physical methods are also widely used.

As far back as prehistoric times, man used natural organic substances (foodstuffs, wood, hides) for his needs. In the course of millennia, mankind gradually learned to process organic substances found in nature: it learned how to produce textiles from the fibres of cotton, wool, flax and silk; convert hides into leather by tanning; extract medicine, dyes and fragrant substances from plants; obtain glycerin and fatty acids from fats; draw out sugar from sugar beat; convert natural rubber into rubber; and process wood, coal and petroleum. Many industries, both light and heavy, are now processing organic substances; they include the oil, gas, petrochemical, coke-by-product, textile, food and pharmaceutical industries.

In the last decades, the production of synthetic high-molecular-weight compounds (polymers) has become especially important: these compounds are used as building materials and for making various household utensils. At first, synthetic materials were regarded only as substitutes for natural ones (rubber, wood, leather, textiles, resins, etc.). But they have now really become "indispensable substitutes", because many tasks of modern technology can be carried out only with new synthetic materials.

I.2. Raw-material Basis of the Organic Synthesis Industry. In the course of many centuries, mankind obtained the necessary organic substances from plant and animal raw material. The variety of industrially-produced organic substances was not very great, while the scale of their production remained rather small.

Since the latter half of the nineteenth century, pit coal became very important as raw material. Coal tar, a by-product of coking, opened the way for the industrial production of benzene, toluene, naphthalene and other aromatics. These substances became the raw material for the synthesis of dyes, medicine and explosives. In the twentieth century, petroleum, whose main components are paraffin hydrocarbons and naphthene hydrocarbons, is becoming increasingly important as raw materials. Natural gas, whose main component is the simplest paraffin hydrocarbon, methane CH_4, has also become important raw material. Organic substances are separated from shale as well. Wood, whose reserves, unlike minerals, are constantly replenished, has lost none of its importance.

It follows that modern industry rests on the processing of hydrocarbon raw material. The simplest organic compounds, hydrocar-

bons, thus became the basis for obtaining various organic substances not only in word, but also in fact. The availability and cheapness of hydrocarbon raw material promoted the rapid development of a new industry, the *organic synthesis industry*, which is the basis for the production of polymeric materials (plastics, synthetic rubber, chemical fibres), dyes, plant protectors, detergents, chemical reagents, medicine, and products of fine organic synthesis.

I.3. Role of Russian Scientists in the Development of Organic Chemistry. Decisions of the CPSU and the Soviet Government on the Development of Chemistry and the Chemical Industry. Our country has every reason to be proud of the great contribution made by Russian scientists to the development of organic chemistry.

There were many prominent organic chemists in Russia before the October Revolution. A. M. Butlerov (1828-1886) laid the foundation of modern organic chemistry by his chemical structure theory in the 1860's; his pupil, V. V. Markovnikov (1834-1904), evolved Butlerov's theoretical principles and revealed the chemical nature of oil by his applied investigations. N. D. Zelinsky (1861-1953) and his pupils made a profound study of the catalytic transformations of hydrocarbons and formed the principles of petrochemistry. N. N. Zinin (1812-1880), M. G. Kucherov (1850-1911), M. I. Konovalov (1858-1906) and A. Ye. Arbuzov (1877-1968) discovered the most important transformations of organic substances, and they later became the basis for new chemical manufacturing processes. F. K. Beilstein generalized the data known in his day in the *Handbuch der organischen Chemie*, which was the beginning of the official registration of organic compounds in *Beilstein's Handbuch* now known to every chemist.

In the West, the discoveries made by Russian chemists are often passed over in silence. However, this did not prevent West European chemical concerns from employing them at their plants. In economically backward tsarist Russia, the chemical industry was developed poorly and the ideas of Russian scientists found almost no application in it.

After the October Revolution, the Communist Party and the Soviet government created the most favourable conditions for chemistry and industry to flourish. A network of research centres was set up, and organic chemists of the old school, such as N. D. Zelins-

ky, A. Ye. Favorsky (1860-1945) and S. V. Lebedev (1874-1934), were given the opportunity to carry out investigations and train young scientists.

What the Soviet Union needed above all was heavy chemical industry which met economic and defence requirements. Such an industry was created in the prewar Five-Year Plan periods. During the Great Patriotic War, it won the competition with the industry of fascist Germany and that of the conquered European countries put at her service. In the postwar years, the chemical industry of the Soviet Union continued to develop, surpassing other industries by its growth rate.

An important constituent of the chemical industry is manufacturing processes based on achievements in organic chemistry. They include those in:

1. Industry of heavy (basic) organic synthesis, which produces hydrocarbons of various types, oxygen-containing organic compounds (alcohols, aldehydes, ketones, acids, ethers and esters), nitrogen-containing organic compounds (nitro compounds, amines, nitriles), halogen-containing organic compounds, and substances containing phosphorus, silicon and other elements. The petrochemical industry is a constituent of the industry of heavy organic synthesis.

Chemicals produced at enterprises of the industry of basic organic synthesis and at petrochemical factories are partially consumed directly (as detergents and solvents), but they are mainly used as raw material for the following industries:

2. Industry producing pesticides and organic fertilizers (urea).
3. Industry producing synthetic resins and plastics.
4. Synthetic rubber industry.
5. Chemical fibre industry.
6. Paint-and-varnish industry.
7. Aniline dye industry.
8. Pharmaceutical industry.
9. Industry producing chemical reagents and highly pure substances.

The decisions of the 25th CPSU Congress for the Tenth Five-Year Plan period earmark great tasks in further developing the chemical and petrochemical industries. Oil extraction will increase to 620-640 million tons, gas output, to 400,000-435,000 million cubic me-

tres, and coal mining, to 790-810 million tons annually. This will provide the industry of organic chemistry with raw material for its further development.

The output of high-octane gasoline, low-sulphur diesel and aviation fuels, and aromatics will be increased by processing petroleum to a greater extent and by enlarging the share of secondary processes.

The output of synthetic resins and plastics will increase 1.9-2.1 times, their quality will improve and their service life will grow. The output of chemical fibres will reach 1.5 million tons annually, and that of synthetic rubber will increase 1.5 times with the production of rubber, which completely substitutes natural rubber, growing at an outstripping rate.

An important task of the chemical industry in the Tenth Five-Year Plan period is the satisfaction of national economic requirements for the products of small-scale chemistry, including chemical additives for polymeric materials, synthetic dyes, textile auxiliary, and conservants. There will be a greater output of chemical articles for domestic needs, film material and other materials for sorting and packing consumer goods. The production of chemicals for agriculture, medicine and other sectors will develop further.

Among the most important tasks are the elaboration of technological processes which will reduce the amount of wastes and provide for their maximum utilization, and the conversion of chemical manufacturing processes into "clean" ones, which are not detrimental to the environment.

Chapter 1

GENERAL PRINCIPLES OF ORGANIC CHEMISTRY

1.1. Specific Features of Organic Compounds. Organic compounds necessarily include carbon, and almost every organic substance also has hydrogen. Many organic substances contain oxygen, nitrogen and, somewhat more rarely, halogens, sulphur and phosphorus. These elements constitute the group of *organogens*, which are found most frequently in the molecules of organic substances. At the same time, almost any element (except noble gases) can be found in the so-called *organoelement compounds.*

At present, we know several million carbon-containing compounds and only several hundreds of thousands of carbon-free compounds. Organic compounds are very diverse, because their molecules can contain tens (and sometimes hundreds and thousands) of atoms which are arranged in a different order. We will learn about this "different order" as we study organic chemistry further.

Typical organic compounds are characterized by definite properties, which differ from those of inorganic substances. The bulk of inorganic compounds is solids having high melting points, while a large part of organic compounds consists of low-melting solids or liquids. Many reactions of organic substances occur more slowly than those of inorganic ones, and transformations often proceed simultaneously in several directions. Organic compounds are destroyed at high temperatures, and many of them are gradually oxidized in the atmosphere. In general, it can be maintained that typical organic substances are of lower strength than typical inorganic ones.

We will learn later that these and other outer distinctions have a deep-going cause: the type of the chemical bond in organic compounds is different from that in inorganic ones.

1.2. Elemental Analysis of Organic Substances. An investigation of any substance begins by obtaining it in pure (individual) form. But it is by far not easy to obtain a pure organic substance. In many cases, it is easier to carry out a reaction than to separate a synthesized product in pure form. The following methods are used for purifying substances.

Recrystallization. This method is widely used also in inorganic chemistry, and therefore it requires no special explanation. The

simplest (although not absolutely reliable) evidence of the purity of a crystalline substance is the constancy of its melting point when crystallization is repeated ("recrystallization to a constant melting point"). The identity of a synthesized substance with another available sample is proven by determining the melting point of their mixture; they are identical if the melting point of the mixture is not depressed.

Distillation. This method is especially used in various forms for purifying organic substances. It applies to simple distillation and vacuum distillation, which allows us to reduce the boiling point by about 100°C (ordinary vacuum, residual pressure is 1-10 mm Hg) or by 200°C (high vacuum, residual pressure is 0.1-0.01 mm Hg) in comparison with distillation at atmospheric pressure. A good purification technique is distillation with water vapour.

Modern distillation devices, rectification columns, make it possible to separate substances whose boiling points differ only by several degrees centigrade.

Sublimation is a purification process used rather rarely; it consists in the employment of the ability of several substances to pass directly from a solid state to a vapour state without becoming a liquid. Sublimation is a very effective technique for purifying a substance.

Extraction is based on the separation of substances by distributing them between immiscible solvents. In the simplest case, extraction is effected by shaking an aqueous solution of an organic substance with such solvents as ether and benzene in a separatory funnel. An organic substance then passes over from an aqueous layer to an organic solvent layer. This is how organic substances are separated from inorganic salts, and various organic substances from one another. There are devices for automatically performing multiple extraction.

Chromatography is based on the differences in the adsorption properties of substances. The foundations of the method were laid by the Russian scientist M. S. Tswett (1903). There are now several variants of chromatography, and the method is often used for purifying and proving the individuality of a substance.

A common principle of all the chromatographic methods is that the mixture to be separated is passed through an *adsorbent*, a substance which is capable of reacting to a different extent with the components of the mixture to be separated. In this case, substances which are being strongly adsorbed move more slowly than those which are being weakly adsorbed, and this is how they are separated. This process occurs most clearly in *chromatographic columns* (Fig. 1.1). Small amounts of substances are separated or identified by *paper chromatography* or in the thin layer of other adsorbents, such as alumina and silica gel (*thin-layer chromatography*).

Gas-liquid chromatography, a technique by which vapours of organic substances are passed through the adsorbent, is especially effective. Many substances which were once said to be individual ones turned out to be mixtures of several components when gas-liquid chromatography was used. Substances purified by this technique are presently the best characteristic of the purity of a substance, although it is not perfect: there are mixtures which cannot be separated by this method.

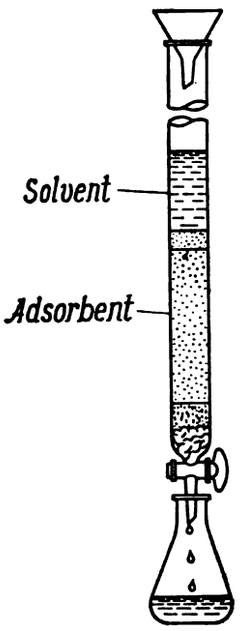


Fig. 1.1. Chromatographic column

All these methods of purifying organic substances are used not only in laboratories, but also in industry.

A pure organic substance is usually characterized by the following constants:

Melting point. The purer a substance, the narrower is its melting range, which is usually 0.5-1.0°C.

Boiling point. Its range for pure substances distilled in rectification columns is tenths of a degree centigrade.

Relative density. It is expressed by the ratio of the mass of a substance at definite temperature (usually 20°C) to the mass of water taken in the same volume at 4°C.

Refractive index. The determination for liquid organic substances is carried out in a refractometer. The refractive index depends on the nature of a substance and also on its purity. This index is the basis for calculating molecular refraction (which will be dealt with in detail at the end of the book).

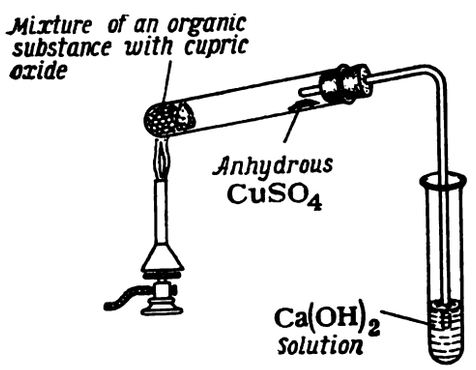


Fig. 1.2. Detection of carbon and hydrogen

Qualitative and quantitative elemental analysis. The investigation of an organic substance isolated in pure form usually begins by ascertaining the elements which constitute it, i.e., by making a *qualitative elemental analysis.*

The qualitative determination of carbon and hydrogen is based on the oxidation of organic substances. In this case, carbon in an organic substance forms carbon dioxide, while hydrogen, water. The substance is mixed with cupric oxide and heated in a test-tube with a gas discharge tube lowered into calcium hydroxide solution (Fig. 1.2). Cupric oxide oxidizes the organic substance. Carbon in it forms carbon dioxide CO_2, which can be detected by the deposit of $CaCO_3$. Water is obtained from hydrogen, and its drops can be

seen in the upper part of the test tube; it can also be detected by the appearance of blue colour of anhydrous copper sulphate placed in the upper part of the test tube.

There are no qualitative reactions for *oxygen*, which is often found in organic compounds, although there are methods of quantitatively determining it.

Nitrogen is detected in an organic substance by fusing a small amount of it with metallic sodium in a test tube: nitrogen is converted into sodium cyanide NaCN. The latter is detected by a reaction of the formation of Berlin blue (the blue colour appears after ferrous and ferric salts are added); this technique is known to us from inorganic chemistry.

The chemical processes which occur when nitrogen is being detected can be expressed by the following equations:

$$Na + C + N \rightleftarrows NaCN$$

$$FeSO_4 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow \underset{\text{Berlin blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

Other elements which may be in an organic molecule are also converted into an inorganic form (they are "mineralized") when they are fused with metallic sodium.

For example, sulphur forms sodium sulphide Na_2S, which is detected by lead nitrate; the black precipitate PbS indicates the presence of sulphur in an organic substance:

$$2Na + S \longrightarrow Na_2S \rightleftarrows 2Na^+ + S^{2-}$$

$$Pb^{2+} + S^{2-} \longrightarrow PbS\downarrow$$

Halogens are converted into the appropriate salts, which produce a precipitate with a silver nitrate solution. Halogens can be detected also by *Beilstein's test*, i.e., by the green colour of the flame in which a copper wire with a halogen-containing substance is put.

Instead of fusing an organic substance with sodium, it can be decomposed by strong oxidizing agents (sodium peroxide, nitric acid, chromic acid mixture). The elements which have passed over to the ionic state are detected then by ordinary reactions which we know from inorganic chemistry.

The *quantitative elemental analysis* of organic substances is performed by burning them (usually in an oxygen stream) in devices which make it possible to quantitatively trap the combustion products. If a substance contains only four elements, i.e., carbon, hydrogen, oxygen and nitrogen, the carbon dioxide and water formed during burning are trapped and weighed (nitrogen is liberated in a free state). Moreover, if there are sulphur, halogens and other elements, additional absorption tubes are connected to the device so as to trap

the compounds of these elements. There are many different variants of quantitatively burning organic compounds. These variants differ by the apparatus used and by the conditions under which substances are burned and the products formed are trapped. Figure 1.3 shows a device for elemental analysis by M. O. Korshun's method that is widely used in the Soviet Union. There are also automatic devices for this analysis.

To reduce the expenditure of a substance and accelerate work, research laboratories practically employ only microdeterminations,

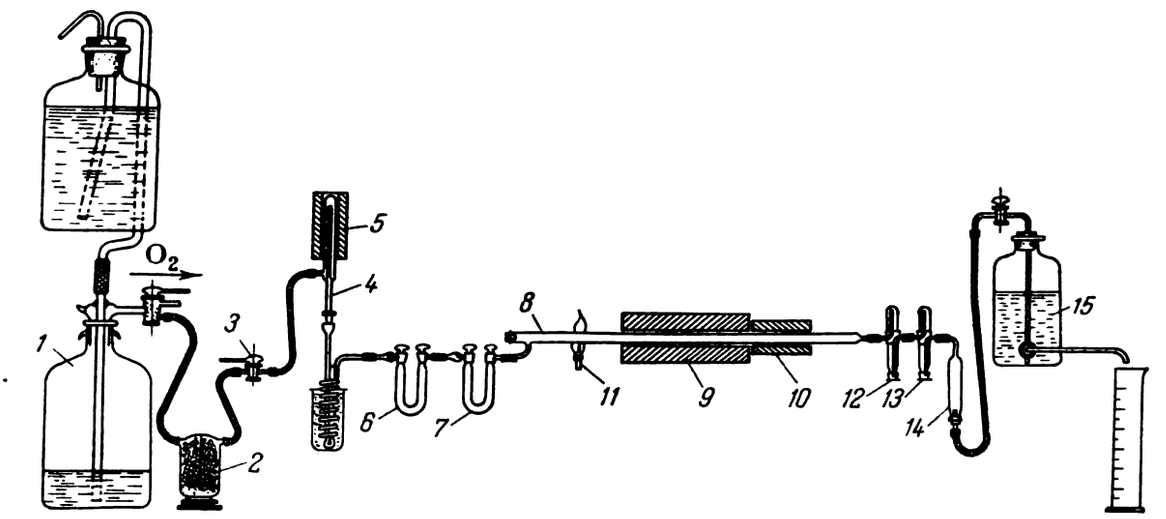


Fig. 1.3. Device for determining carbon and hydrogen by M. O. Korshun's technique:

1—gas meter; *2*—drying bottle; *3*—stopcock; *4*—device for purifying oxygen; *5*, *9*, *10*—electric furnaces; *6*, *7*—devices for absorbing H_2O and CO_2, which are formed after oxygen purification; *8*—combustion tube; *11*—gas burner; *12*, *13*—devices for absorbing H_2O and CO_2, which are formed when a test sample burns up; *14*—insulating tube; *15*—aspirator

i.e., work is done in devices which make it possible to use 3-5 mg of a substance for analysis.

Suppose a portion of 4.52 mg of an organic substance consisting of carbon, hydrogen and oxygen was taken for an elemental microanalysis, and 9.18 mg of CO_2 and 2.88 mg of H_2O were obtained after it was burned. The combustion products contain the entire carbon and hydrogen which were in the portion of the substance to be analysed. These data are used to calculate the amounts of the elements in the portion (2.51 mg of carbon and 0.32 mg of hydrogen), and then also their percentage. In this case, 55.6 per cent of carbon and 7.08 per cent of hydrogen are obtained. Oxygen constitutes the remaining amount (37.3 per cent). To switch over from mass fractions of the elements to their atomic ratios, it is necessary to divide the percentage by the atomic masses of the respective elements. The numbers 4.63 C : 7.08 H : 2.33 O are thus obtained. Dividing this ratio by the smallest of these numbers, we obtain a more convenient

ratio of 1.99 : 3.05 : 1.00 or, in round figures, the whole numbers of 2:3:1.

The numbers express the ratio between the atoms of C, H and O in a molecule of the substance being analysed, i.e., its simplest formula can be written as C_2H_3O. But this does not mean that that is exactly the composition of the molecule, since it can be doubled or tripled; in general, it can correspond to the formula $(C_2H_3O)_n$.

To establish the molecular formula, it is necessary to determine the *relative molecular mass* (*molecular weight*) of a substance. Many methods can be used for this purpose, e.g., by vapour pressure measurement or the cryoscopic method. If we receive a molecular mass of the order of 90 for our example, we can regard the formula $C_4H_6O_2$ as a molecular one.

1.3. Isomerism. In studying inorganic compounds, the molecular formula serves in most cases as an accurate "visiting card" of a compound. The formula H_2SO_4 is undoubtedly the formula of sulphuric acid, $NaHCO_3$, that of sodium bicarbonate, and so forth. But things are different in organic chemistry: various substances can have the same molecular formula. For example, the formula C_2H_6O applies to two substances: a gas called dimethyl ether and a liquid known as ethyl alcohol. The formula C_4H_8O applies to 21 substances!

Different substances having the same molecular formula are known as isomers, while the phenomenon itself is called isomerism (from the Greek "isomeres", which means "consisting of equal parts" or "equally divided").

Why are isomers different? Since the composition of their molecules is the same (this follows from the definition of isomerism itself), the cause of the difference can be found only in the different arrangement of the bonds of atoms in a molecule. The phenomenon of isomerism thus forces us to look further, ascertaining the details of the inner structure of molecules of organic substances, because the establishment of the molecular formula is not enough. Therefore, the phenomenon of isomerism (which was discovered as early as at the beginning of the last century) was a constant stimulus for developing the theoretical concepts of organic chemistry.

Owing to the existence of isomers, simple molecular formulas common to inorganic chemistry are not enough. Therefore, one of the most important prerequisites for successfully studying organic chemistry is the most rapid assimilation of a new type of formulas: structural formulas. We will become acquainted with them for the first time in one of the immediately following sections.

1.4. Original Concepts of the Nature of Organic Compounds. Any science starts by a classification of the collected factual material. In chemistry, the matter in question is obviously above all the classification of chemical compounds. Until the eighteenth century, chemists made no distinction between mineral and organic substan-

ces. For example, the term "salts" was applied to colourless water-soluble crystalline substances: inorganic common salt and other salts were classified together with such organic substances as succinic and oxalic acids. The term "oils" was applied to all dense liquids, including not only vegetable oils, but also "oil of vitriol" (a name which is still used in technological processes for concentrated sulphuric acid), "cream of tartar", and zinc chloride, which also readily absorbs moisture from the atmosphere and turns into a dense liquid. Volatile liquids were regarded as spirits (from the Latin "spiritus", meaning "spirit"). In conformity with such a definition, ethyl alcohol, stannic chloride, hydrochloric acid and ammonia spirit were regarded as spirits. The last term, ammonia spirit, is used even today.

By the middle of the eighteenth century, a considerably large number of substances, which had many common properties and a similar composition, but which substantially differed from mineral (inorganic) substances, were extracted from plant and animal organisms. Substances of plant and animal origin became known as *organic* substances. At the beginning of the nineteenth century, the famous Swedish chemist Berzelius (1779-1848) drew a clear-cut line between mineral and organic substances in his study guide in chemistry. According to him, the basic difference was that organic substances were supposedly obtained only in living organisms with the participation of a mysterious "vital force", while such synthesis allegedly cannot be effected in the laboratory.

The concept of the need for the "vital force" to participate in the creation of organic compounds became known as *vitalism* (from the Latin "vita", meaning "life"). It was the same manifestation of idealism as belief in the existence of a "soul" in biology. The vitalistic views were proven to be wrong as early as in the first half of the nineteenth century by synthesizing many organic substances. Important landmarks in this respect were the production of urea from an inorganic substance called ammonium cyanate (Wöhler, 1828), the synthesis of fats (Berthelot, 1854) and the synthesis of sugary substances (Butlerov, 1861).

The first attempts to explain the nature of organic compounds were made in the 1820's and 1830's by Berzelius in his dualistic theory, or the theory of radicals. The name "dualistic" (from the Latin "duo", meaning "two") is connected with the fact that Berzelius thought organic substances were made out of two parts. He called these parts radicals, and hence the second name of his theory. It was believed that radicals were the "genuine elements of organic chemistry", and that they could pass over from one compound to another without any change. These concepts of Berzelius' correctly reflect one of the distinguishing features of organic molecules, i.e., the presence of definite stable atomic groups in them that remain

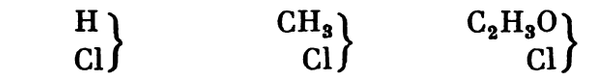
unaffected in chemical transformations. But Berzelius was wrong in believing that this stability was perfect and in insisting that radicals could be isolated in a free state. His concepts of the role of electric charges in organic molecules were also naive. However, knowing quite well that organic radicals and ions are intermediate particles which really exist in the course of transformations of organic substances, we cannot condemn these views of Berzelius' so resolutely as was done at the turn of this century.

In the 1840's and 1850's, the theory of radicals was replaced by the *theory of types*, which was associated mainly with the French scientist Gerhardt. He regarded all the organic compounds as derivatives of the simplest substances: hydrogen, hydrogen chloride, water and ammonia:

Type of hydrogen

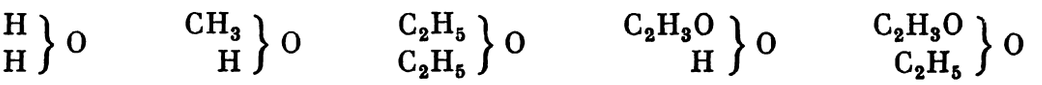
Hydrogen — Methane — Ethane — Acetaldehyde

Type of hydrogen chloride



Hydrogen chloride — Methyl chloride — Acetyl chloride

Type of water



Water — Methyl alcohol — Diethyl ether — Acetic acid — Ethyl acetate

By using such an approach, formulas were obtained for many organic compounds that were similar to modern structural formulas. But the advocates of the type theory gave it a completely different content: they maintained that the formulas of the type theory were simply conversion ones. Many different formulas were written for the same substance, depending on the chemical reactions which the formulas were intended to express. These advocates held that the inner structure of molecules was fundamentally incognizable, thus taking the stand of agnosticism, a false philosophy which sets limits to human cognition.

Besides the main theories, there were many varieties of them. The distinctions seemed so important for the authors of these variants that they often acknowledged only their own interpretation, rejecting all the others. As a result, it was often difficult for chemists to understand each other. The state of organic chemistry in the first half of the nineteenth century is vividly described by Hjelt in his book *Geschichte der organischen Chemie von ältester Zeit bis zur Gegenwart*, where he wrote: "In the 1840's and 1850's, real anarchy reigned

supreme in this field, throwing many chemists into despair and retarding the quiescent development of science. The atomic weights of Berzelius, Dumas and Gerhardt-Laurent, and also Gmelin's equivalent weights were used without any discrimination. Therefore, the chemical formulas of organic compounds were variegated and unattractive ... . If the formula H_2O_2 was seen somewhere, it was necessary to guess whether it stood for water or hydrogen peroxide. The formula C_2H_4 stood either for marsh gas (methane) or ethylene, depending on the camp to which its author belonged."

In the 1850's, "anarchy" in chemistry gradually began to ebb. As a result of the works by Frankland and Kekulé, the concept of *valence* was asserted in chemistry. In particular, Kekulé evolved the concept of the tetravalence of carbon. Owing to the works by Cannizzaro, the question of atomic and molecular masses, or of equivalence, became clear.

In 1860, more than 140 prominent chemists from various European countries assembled at the international congress in Karlsruhe, Germany. At the congress, the participants unanimously agreed on the fundamental concepts of chemistry (the atom, the molecule, the equivalent), and acknowledged Avogadro's law; the correct values of the atomic masses of the elements then began to be used. All these scientific achievements prepared the conditions for a new stage in the development of organic chemistry: the appearance of the theory of the chemical structure of organic compounds.

1.5. Theory of the Chemical Structure of Organic Compounds. The chemical structural theory was worked out by the great Russian chemist A. M. Butlerov (1828-1886). He formulated the basic principles of his theory in 1858-1861. The structural theory is of certain difficulty for us, because he did not formulate the principles of his theory point by point in one place: they permeate the entire creative scientific work by Butlerov and his pupils.

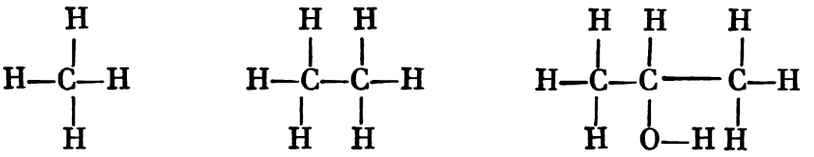
1. The atoms in organic molecules are bound with one another by chemical forces in a definite order. It is this order that Butlerov called the "chemical structure". In his day, these forces were called "valence forces" only in a general manner, but it has now been ascertained that they have an electronic nature (see Sec. 1.8).

2. The structure can be studied experimentally by employing the chemical methods of analysis and synthesis. To ascertain the structure, wide use is now also made of physical methods: various types of optical spectroscopy, nuclear magnetic resonance, mass spectrometry, X-ray analysis, electron diffraction, and the determination of dipole moments.

Physical methods, especially X-ray analysis and electron diffraction, make it possible to determine the real position of every atom in a molecule, i.e., to obtain its photograph, as it were. This arrangement is matched with that found by a purely chemical technique.

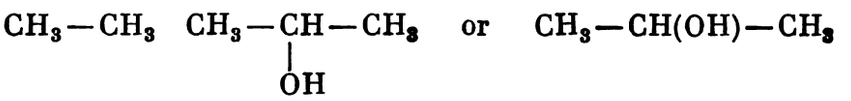
Therefore, we often speak simply of the *structure of molecules*, dropping out the adjective "chemical", which Butlerov used without fail.

3. Structural formulas express the order of the chemical bond of atoms. In these formulas, the symbols of elements are connected by lines, which conventionally represent the chemical bond, e.g.,



Methane CH_4 | Ethane C_2H_6 | Isopropyl alcohol C_3H_8O

Expanded structural formulas (i.e., formulas in which every atom and every bond are denoted) are difficult to read when a molecule is slightly complex. Therefore, it is necessary from the very beginning to become accustomed to condensed structural formulas, e.g.,



Ethane | Isopropyl alcohol

As the examples show, in condensed structural formulas, the atoms and groups which are directly bound with the carbon atom are placed next to it, and then a line is drawn and another carbon atom with the substituents standing next to it is written. To reduce a structural formula further, the lines are sometimes dropped out altogether, e.g., $CH_3CH(OH)CH_3$.

In constructing structural formulas of organic compounds, account must be taken of the valence of the elements, or organogens, that is found empirically. For example, the valence of carbon is 4; hydrogen, 1; oxygen, 2, and halogens, 1. Nitrogen, sulphur and phosphorus can be in different valence states.

4. Every substance has a definite structural formula which expresses the order of the chemical bond of atoms in a really existing molecule. This principle is profoundly materialistic and philosophically correct: an object which really exists in nature, a molecule, constitutes the basis, and the structural formula must express this object as accurately as possible. All the modern "improvements" in writing structural formulas of organic substances, such as the introduction of notations of electron pairs, arrows, dots and charge signs into them, are intended to meet that requirement. This brings the formula and a real molecule into better conformity, i.e., this conforms to the principles of the structural theory.

5. The atoms bound in a molecule mutually affect one another: the properties of every atom in a molecule depend not only on the

nature of the atom, but also on its environment. We will constantly come across the mutual influence of atoms throughout this textbook of organic chemistry. Meanwhile, let us confine ourselves to a very simple example: the hydrogen atom is contained in the water molecule and in the hydrogen chloride molecule, but its properties in both substances are very different.

6. The physical and chemical properties of organic compounds are determined by the composition and structure of their molecules. In Butlerov's day, only the *chemical* structure, i.e., the order of the chemical bond of atoms, could be determined. At present, we can determine also the *three-dimensional* structure and the distribution of electric charges, i.e., the *electron* structure. All the three structural characteristics are important when the properties of organic compounds are being considered.

The chemical structural theory has made it possible to understand the nature of isomerism: *the molecules of structural isomers have the same composition, but differ by the order of the atomic bond (by the chemical structure)*. For instance, the formula C_2H_6O, which was mentioned earlier (p. 26), is valid for two different substances:

$CH_3—O—CH_3$	$CH_3—CH_2OH$
Dimethyl ether	Ethyl alcohol

Butlerov did not confine himself only to the theoretical explanation of isomerism on the basis of the structural theory. He also carried out a series of experiments, confirming theoretical predictions by obtaining isobutane and tertiary butyl alcohol.

1.6. Electron Shell of an Atom. Owing to the achievements made in chemistry and physics, we now know that chemical phenomena are connected with processes occurring in the electron shell of atoms. The electronic structure of atoms should be known to us from textbooks of physics and inorganic chemistry, and it will be mentioned only briefly here. An atom consists of a positively charged nucleus which is surrounded by an electron shell having a negative charge. It was believed at first that an atom could be represented as a miniature solar system in which the nucleus plays the role of the Sun, while the planets, i.e., electrons, move around it. But it was soon learned that the laws of quantum mechanics, which operate in the world of fundamental particles (protons, neutrons, electrons, etc.), substantially differ from "ordinary" physical laws.

For instance, according to quantum mechanics, the electron simultaneously possesses the properties of a particle and those of a wave. Instead of a physical point, an *electron cloud* is considered, and the nature of the cloud is determined by four *quantum numbers.*

The dimensions of an electron cloud are determined by the *principal quantum number* (n), which can assume the integral values of

1, 2, 3, and so forth, in conformity with the period number. The principal quantum number simultaneously defines the energy of the electron, its *energy level.*

The shape of an electron cloud is determined by the *additional* (*azimuthal*, *orbital*) *quantum number* (l), which can have values

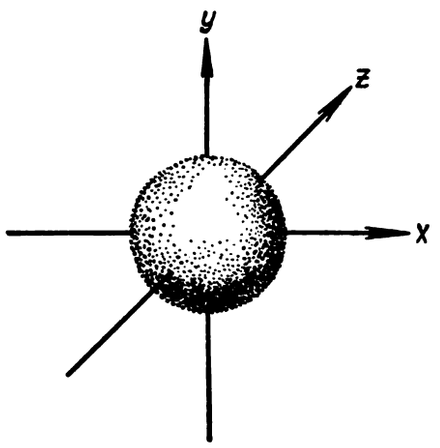


Fig. 1.4. Spherical *s*-orbital

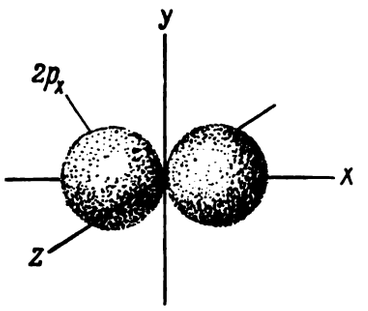


Fig. 1.5. *p*-Electron cloud

ranging from 0 to $n - 1$. The value of $l = 0$ is for the *spherical* electron cloud in the centre of which is the atomic nucleus (Fig. 1.4); such electrons are known as *s*-electrons. The value of $l = 1$ is for the electron cloud which is in the form of two ellipsoids (for clarity,

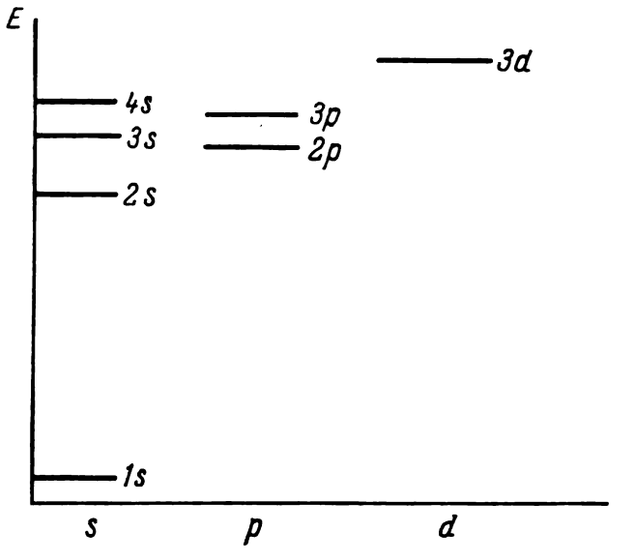


Fig. 1.6. Energy of electron states

they are often represented as "dumb-bells"), between which is the atomic nucleus (Fig. 1.5); such electrons are known as *p*-electrons. However, the two given states of electrons, which are within the limits of a single energy level, somewhat differ from one another

by their energies (they are at different *energy sub-levels*) and the energy of *p*-electrons is somewhat greater than that of *s*-electrons (Fig. 1.6).

When the principal quantum number is 3, electron clouds of a more complex shape appear. Such clouds are of little importance for organogen elements, and therefore we will not consider them.

The *magnetic quantum number m* characterizes the spatial orientation of ellipsoidal orbitals of the second-period elements: the magnetic quantum numbers in this case are denoted by subscripts with the letter *p* (i.e., p_x, p_y, p_z), connecting them with the orientation of ellipsoidal *p*-orbitals by three coordinates.

The quantum numbers of *n*, *l* and *m* thus determine the spatial regions where electrons are "allowed" to reside. Such spatial regions around a nucleus became known as *orbitals of electrons*. They can be either *occupied* (filled with electrons) or *unoccupied*.

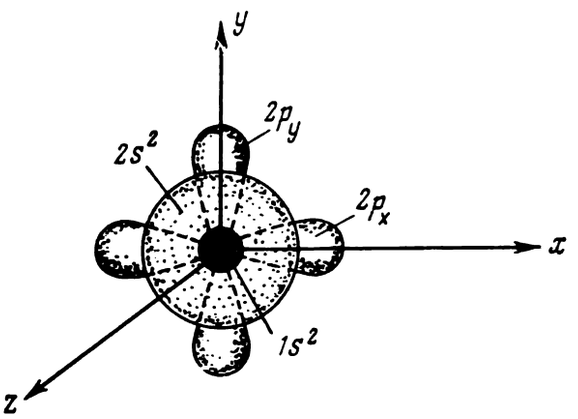


Fig. 1.7. Electron orbitals of the unexcited carbon atom

The fourth quantum number, the *spin quantum number* (*s*), characterizes the rotation of the electron around its own axis. The electron can rotate, like a top, clockwise and counterclockwise. The electrons which have the same quantum numbers of *n*, *l* and *m* (electrons which occupy the same electron orbital), but which differ in spin, constitute the *electron pair*. We will learn later that it is precisely the electron pairs which are responsible for the formation of bonds in the molecules of organic substances.

According to *Pauli's principle* no two electrons in a given atom can have the same four quantum number.

Table 1.1 gives the electronic states of elements of the first and second periods of the periodic system. In the table, every electron is denoted by an arrow, and the opposite directions of arrows indicate opposite spins. Every orbital of electrons is conventionally represented as a rectangle, and the arrangement of the rectangles at different levels suggests the energies of the respective orbitals.

In the table, we will see that the number of unpaired electrons and valence are in conformity: one for hydrogen, lithium and fluorine; two for oxygen, and three for nitrogen. But there is an exception: boron has one valence electron, but its ordinary valence is three; beryllium has no unpaired electrons, but its valence is two. Carbon has two unpaired electrons (Fig. 1.7), and this also does not conform with the ordinary tetravalence of the element.

TABLE 1.1. **Electronic States of Atoms**

Element	Atomic number	Electron distribution: *K*-layer $n=1$ $m=0$ $l=0$	*L*-layer ($n=2$): $l=0$ $m=0$	$l=1$ $m=-1$	$l=1$ $m=0$	$l=1$ $m=+1$	Conventional registration of electron distribution
Hydrogen	1	↑					$1s$
Helium	2	↑↓					$1s^2$
Lithium	3	↑↓	↑				$1s^22s$
Beryllium	4	↑↓	↑↓				$1s^22s^2$
Boron	5	↑↓	↑↓	↑			$1s^22s^22p$
Carbon	6	↑↓	↑↓	↑	↑		$1s^22s^22p^2$
Nitrogen	7	↑↓	↑↓	↑	↑	↑	$1s^22s^22p^3$
Oxygen	8	↑↓	↑↓	↑↓	↑	↑	$1s^22s^22p^4$
Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	$1s^22s^22p^5$
Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^22s^22p^6$

1.7. Valence States of Carbon. Hybridization. To bring the electronic structure of the carbon atom into conformity with the valence of the element, the concept of carbon atom excitation is used:

$$C \longrightarrow C_{excit.}$$

In an excited state, the carbon atom has four unpaired electrons and, consequently, can exhibit tetravalence. But there is another

contradiction: the four valence electrons differ from one another by their state [one 2*s*- and three 2*p*-electrons (Fig. 1.8)], while it has been proven experimentally that all the four valencies of carbon are the same, and are at tetrahedral angles of 109°28′ relative to one another. To bring the theoretical consideration into conformity

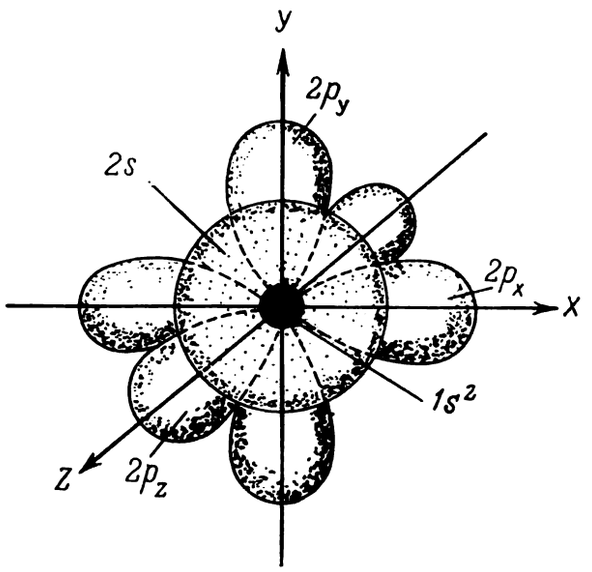


Fig. 1.8. Electron orbitals of the excited carbon atom

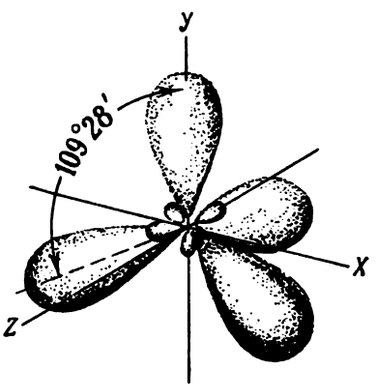


Fig. 1.9. Electron orbitals of the carbon atom in the state of sp^3-hybridization

with empirical data, Pauling introduced the concept of the hybridization of atomic orbitals, i.e., the "mixing" of the spherical *s*- and the elliptic *p*-orbitals. The carbon atom can have three valence states with different types of hybridization:

sp^3 *Hybridization*, when one *s*- and three *p*-orbitals mix together. There will then be four equivalent electron orbitals which are arranged at tetrahedral angles relative to one another (Fig. 1.9).

sp^2 *Hybridization*, when one *s*- and two *p*-orbitals mix together. There will then be three hybrid orbitals whose axes are oriented, all on the same plane, at mutual angles of 120°. The direction of the unhybridized *p*-orbital is perpendicular to the plane of the hybridized ones (Fig. 1.10).

sp Hybridization. In this case, one *s*- orbital and only one *p*-orbital mix together and two hybrid orbitals are formed. They lie in opposite directions from the carbon atom nucleus on a straight line. The two remaining unhybridized *p*-orbitals are arranged on mutually perpendicular planes (Fig. 1.11).

1.8. Electronic Nature of the Chemical Bond. Many inorganic compounds have an ionic (electrovalent) bond between atoms. Moreover, this bond is known to be engendered by the transfer of electrons from one atom to another: as a result, a positively charged ion

(metals, hydrogen), a cation, is formed, and it becomes bound with a negatively charged ion (hydroxyl, acid residues), an anion, by forces of electrostatic attraction. In this case, stable electron shells are formed, corresponding to the electron configuration of rare

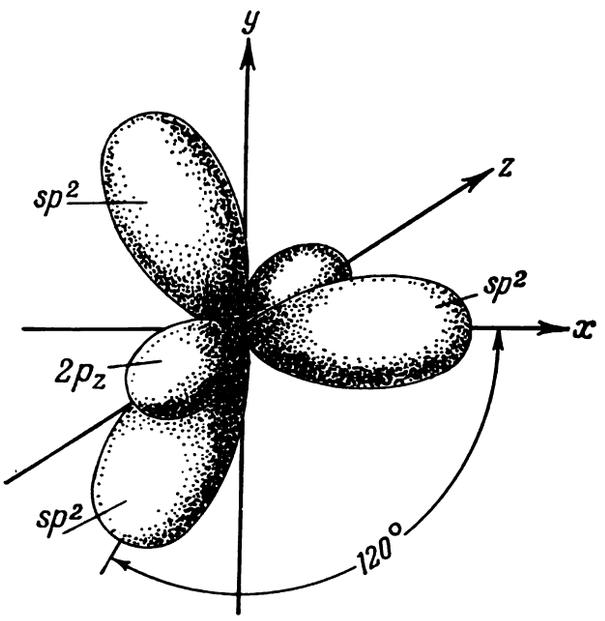


Fig. 1.10. Electron orbitals of the carbon atom in the state of sp^2-hybridization

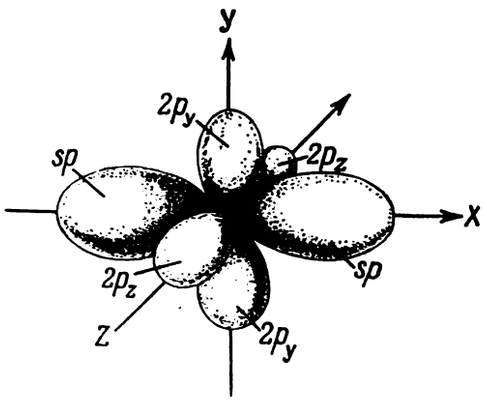


Fig. 1.11. Electron orbitals of the carbon atom in the state of *sp*-hybridization

gases: helium (two electrons on the *K*-shell), neon (eight electrons on the *L*-shell, *octet*), and others.

The absence of dissociation into ions by most organic compounds and their other properties gave rise long ago to the assumption that the type of bond in organic molecules is different, this bond is known as the *covalent bond*, and it is effected not by transferring, but *by sharing electrons*. The simplest example of the covalent bond is the formation of the molecule of hydrogen from its atoms. Each of the hydrogen atoms has one electron. If two hydrogen atoms whose electrons have opposite spins approach one another, their electron density is combined: by sharing their electrons, both atoms acquire a stable electron shell of the nearest rare gas, helium:

$$H\cdot + \cdot H \longrightarrow H{:}H$$

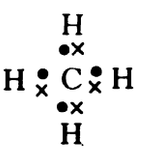
Electrons with opposite spins form the bonding electron pair, and the process of hydrogen molecule formation may be represented also in the following way:

$$H\uparrow + \downarrow H \longrightarrow H\uparrow\downarrow H$$

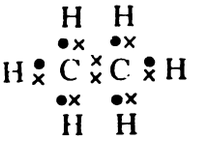
In passing over from a "dot" model of the electron to the concept of the electron cloud, we will obtain an ellipsoid in which the elec-

tron density between nuclei is greater than in other places, and this holds positively charged nuclei together (Fig. 1.12).

That is also how covalent bonds are formed in organic molecules, e.g., in methane CH_4 and ethane C_2H_6:



Methane



Ethane

For clarity, carbon valence electrons proper are denoted by crosses, and the electrons which formerly belonged to hydrogen atoms, by dots (this is done only for illustrating the technique of bond formation, but in fact the electrons are undistinguishable). Owing to electron sharing, the carbon atom now has eight electrons on the outer orbital, like neon, while each of the four hydrogen atoms has two, like helium. Each of the atoms has thus attained a stable electronic state which corresponds to the noble gas.

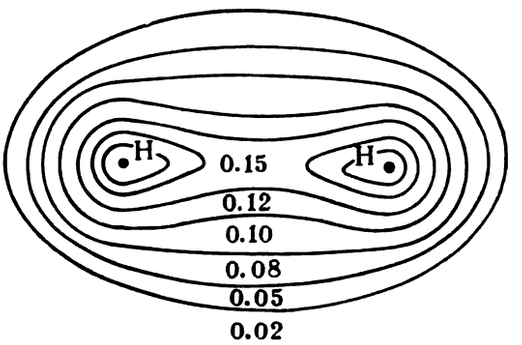
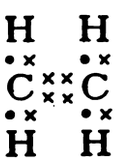


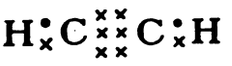
Fig. 1.12. Distribution of electron density in the hydrogen molecule

Carbon in methane and ethane, having a tetrahedral configuration, is in a state of sp^3 hybridization (Fig. 1.13).

Besides *single bonds* (they are known as σ-*bonds*), in the formation of which an electron pair participates, organic molecules may also have *double and triple bonds*: they are formed by two and three electron pairs, respectively, e.g.,



Ethylene



Acetylene

Carbon in such compounds is found in a different valence state (sp^2 and sp hybridizations, respectively).

Various types of covalent bonds in organic compounds will be gradually discussed in greater detail.

But one may ask why carbon forms covalent bonds by electron sharing, and why it does not tend to form bonds by giving away or gaining electrons. Having four valence electrons, the carbon atom should gain another four electrons to form a stable octet. But after

gaining the first electron, carbon would become negatively charged, and ever greater energy would be required for every new electron to approach an anion of small size (the radius of the carbon atom

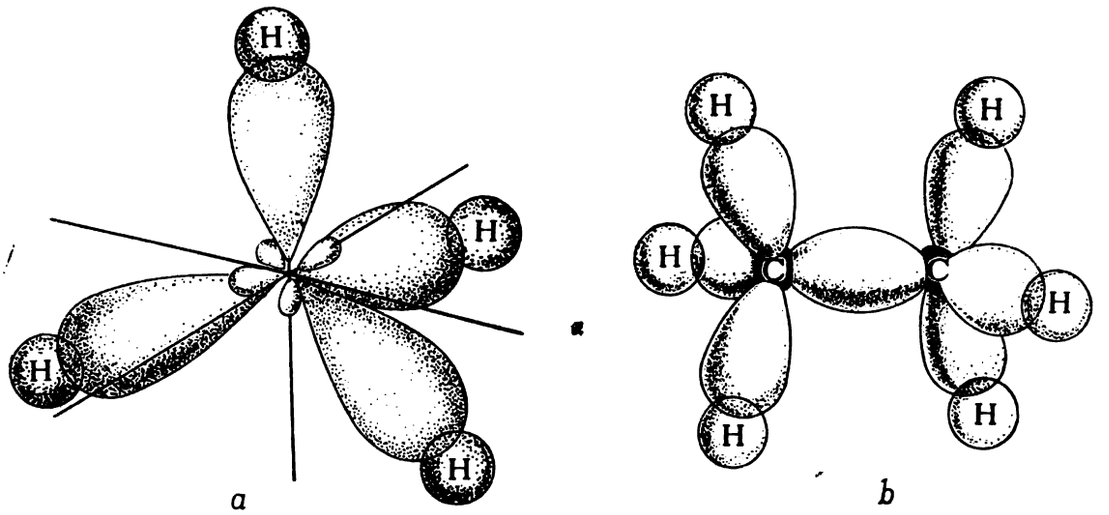


Fig. 1.13. Model of the σ-bond in methane (*a*) and ethane (*b*)

is small): therefore, the formation of the ion C^{4-} is extremely disadvantageous. It is likewise difficult for the four electrons to be separated, and the ion C^{4+} would then be formed, because every following electron must go away, overcoming the attraction of the remaining cation. The conditions for the formation of covalent bonds by electron sharing, when charges do not originate, are far more favourable.

A different approach to the theoretical treatment of organic structure is increasingly used at present: the molecular orbital theory. Instead of localized (fixed) electron pairs, the interaction of all the valence electrons with all the nuclei is essentially investigated. In many cases, such an approach makes it possible to better understand the properties of organic compounds. But the clear-cut concept of chemical bond is somewhat lost, and this is too difficult for a beginner in organic chemistry. There are still no fundamental courses in organic chemistry wholly based on the molecular orbital theory.

1.9. Characteristics of Covalent Bonds and the Methods of Determining Them. A great achievement in modern science is that an exact numerical description can be given for every specific bond. It includes geometric parameters, i.e., bond lengths, bond (or valence) angles and bond energy, and also electronic parameters, i.e., polarity and polarizability (see Table 1.2).

The *bond length*, the internuclear distance depends on the nature of atoms and of the bond between them (whether it is single, double or triple). The bonds become shorter when their order increases.

The bond lengths are usually within the limits of 0.1-0.2 nm [1 nm (nanometer) is equal to 10^{-9} m, or 10 Å].

The *bond angle* is the angle between the directions of the bonds being formed by a multivalent atom. For example, in a water molecule, two O—H bonds are at an angle of about 100° relative to one another, and this is the bond angle of the oxygen atom. The nitrogen atom in the trivalent state has three bonds directed towards the angles of the base of a trihedral pyramid, at whose vertex is nitrogen. The bond lengths and bond angles in the water molecule and

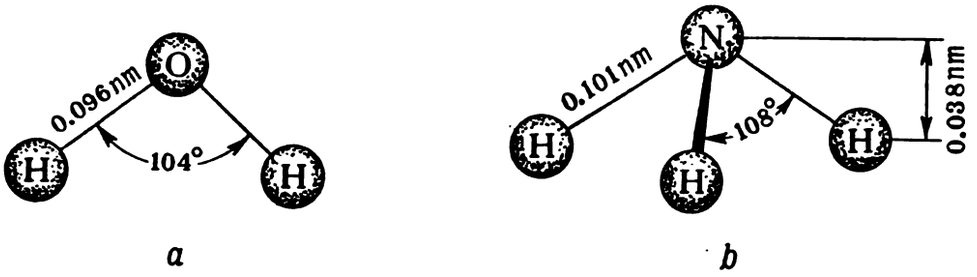


Fig. 1.14. Bond lengths and bond angles in the water molecule (*a*) and the ammonia molecule (*b*)

in the ammonia molecule are exemplified in Fig. 1.14. The bond angle of the carbon atom depends on its valence state, i.e., on the type of hybridization.

The geometric parameters of molecules are determined by X-ray analysis and electron diffraction. In these methods, X-rays passing through a substance, or electrons flowing through it, produce a diffraction pattern, which makes it possible to calculate interatomic distances and bond angles. Both methods supplement one another quite well: X-ray analysis has great precision (interatomic distances are measured with a precision of ± 0.0001 nm), but it cannot be used to determine the position of hydrogen atoms. Electron diffraction is less precise (0.001 nm), but it establishes the position of hydrogen atoms. X-ray analysis is used mainly for crystalline substances, while electron diffraction, for gases.

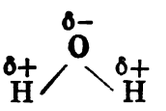
Interatomic distances and bond angles can be determined also by *neutron diffraction*, i.e., they can be calculated from spectral data. All these methods have made it possible to obtain reliable data on the geometric structure of organic compound molecules. The data confirm and specify what chemists had long arrived at by their methods, i.e., by Butlerov's chemical structural theory and by van't Hoff's stereochemical hypothesis.

Bond energy is a quantity which characterizes the bond strength. Energy is always liberated when the chemical bond is being formed; it is known as bond energy and is measured in kilojoules per mole (kJ/mole). To break the bond, a definite amount of energy must be

consumed: apparently, the greater the bond energy, the stronger is the bond and the more difficult it is to rupture it.

The best way of obtaining information on bond energies is by using *thermochemical data*, i.e., information on the thermal effects of reactions. These data are obtained practically in most cases as *heats of combustion*, i.e., the thermal effect which accompanies the complete combustion of an organic compound down to the oxides of the elements constituting it (CO_2, H_2O, SO_2); nitrogen, bromine and iodine are isolated in a free state, while chlorine forms HCl. Combustion is effected in *calorimeters*, i.e., devices consisting of durable metallic vessels for burning a substance under oxygen pressure; the amount of heat evolved is taken into account by the elevation of temperature in a special water jacket of a vessel. The data obtained are used for calculating the *heats of formation* of compounds from the atoms which constitute their elements; a switch-over is then made from formation heats to bond energies. For example, the heat of formation of methane is 1660 kJ/mole. Since four C—H bonds originate when methane is being formed, the energy required for each of them is 1660 : 4 = 415 kJ/mole. The difference in the heats of formation of two neighbouring members of a paraffin series is about 1180 kJ/mole; this value corresponds to the *heat of formation of the group* CH_2, i.e., to the formation of an additional C—C bond and two C—H bonds. Subtracting the energy of two C—H bonds from the foregoing value, we can obtain the energy of the C—C bond (ca. 350 kJ/mole). The energy of other bonds is also found similarly.

Bond polarity indicates both the nature of distribution of electrons between bonded atoms and the charge on the atoms. Atoms of various elements have a different affinity for electrons: some of them, like lithium and sodium, readily give away electrons, while others, like fluorine and chlorine, readily gain them. The tendency to gain electrons (*electronegativity* of atoms) grows in the periodic table from left to right and goes up the period. Atoms act toward the electron pair bonding them also in conformity with their electronegativity: one of the partners of a bond can be rather "indifferent" to electrons and give his partner the opportunity to gain possession of the bonding electron pair by "more than one-half". It is not difficult to see what this will cause: the symmetry in the distribution of charges will be upset, i.e., a part of the molecule will become positively charged, while the remaining part, negatively. In general, these charges will not be equal to the total electron charge. Such partial charges are denoted by the symbols $\delta+$ and $\delta-$. The simplest example is the water molecule:



Polarity is a very important property of bonds, because it is precisely the presence of one charge or another on an atom that determines its reactivity. Polarity affects also physical properties. For instance, it is exhibited most clearly in the existence of dipole systems, whose polarity can be measured experimentally and expressed as the dipole moment (μ), i.e., the product of the size of a charge e by the distance between charges (Fig. 1.15). Using electrostatic units (4.8×10^{-10}) to measure the size of a charge, we obtain the order of the value of the dipole moment D, 10^{-18}, in the cgs system of units when the distance between charges is 0.1 nm. This value is taken as the unit of the dipole moment D (debye).

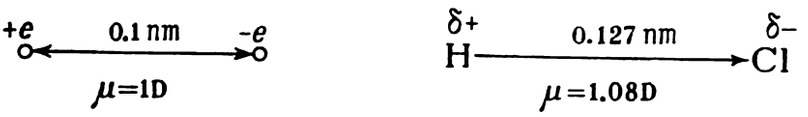


Fig. 1.15. Examples of dipole systems

The *polarity* of covalent bonds is experimentally determined above all from *dipole moments*. Let us explain this by taking a simple example. The experimentally determined dipole moment of hydrogen chloride gas is 1.08 D, while the distance H—Cl is 0.127 nm. Using the relationship between the dipole moment, charges and the distance between them $\mu = e \cdot r$, we can calculate the value of the charges on the atoms of hydrogen and chlorine:

$$e = \frac{\mu}{r} = \frac{1.08 \times 10^{-18}}{0.127 \times 10^{-7}} = 0.85 \times 10^{-10} \text{ esu}$$

Thus, in hydrogen chloride gas, less than one-fifth of the electron charge (0.85 : 4.8) is on atoms; the bond H—Cl in this gas is covalent to a considerable extent, and it becomes ionic only when the molecules get into a medium having a high dielectric constant, say, water.

Besides polarity, which is an inherent feature of bonds in a static state, every bond also possesses definite *polarizability*, or the ability to change (increase) its polarity under the action of the external electromagnetic field. Such a field can be created also by a molecule which approaches during a chemical reaction, and polarizability therefore determines chemical properties to a considerable extent.

In Table 1.2, the physicochemical characteristics of various covalent bonds are compared. These data relate to standard bonds, and they can change noticeably as a result of the action of neighbouring atoms (neighbouring bonds): the mutual influence of atoms is expressed precisely in this. The atom forming the positive end of the dipole stands first throughout the table.

TABLE 1.2. **Lengths, Energies, Polarities and Polarizabilities of Covalent Bonds**

Type of bond	Length, nm	Energy, kJ/mole	Polarity, debye units	Polarizability, cc
C—C	0.154	348	0	1.3
C=C	0.133	620	0	4.2
C≡C	0.120	810	0	6.2
C—N	0.147	290	0.5	1.6
C=N	0.127	615	1.4	3.8
C≡N	0.115	880	3.1	4.8
C—O	0.143	340	0.7	1.5
C=O	0.121	710	2.4	3.3
C—F	0.140	485	1.4	1.4
C—Cl	0.176	330	1.5	6.5
C—Br	0.191	280	1.4	9.4
C—I	0.212	240	1.3	14.6
H—C	0.109	415	0.4	1.7
H—O	0.096	465	1.5	1.7
H—S	0.134	340		4.8
H—N	0.101	390	1.3	1.8
N—N	0.148	160	0	2.0
N=N	0.124	420	0	4.1
N≡N	0.109	950	0	
N—O	0.137	200	1.0	2.4
N=O	0.122	400	3.0	4.0

1.10. Types of Organic Reactions. Organic reactions, like inorganic ones, can be classified by their results, and a distinction must be made between:

substitution reactions:

$$CH_4 + Br_2 \longrightarrow CH_3Br + HBr$$

addition reactions:

$$CH_2=CH_2 + Br_2 \longrightarrow BrCH_2-CH_2Br$$

elimination reactions:

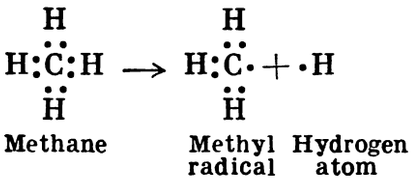
$$BrCH_2-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$$

A special, important type of addition reactions is the interaction between two (or several) organic molecules, which make a carbon skeleton more complex. Such transformations are known as reactions of *polymerization* and *condensation*.

In modern organic chemistry, organic reactions can be classified by their mechanisms. In studying the reaction mechanisms, we ascertain the order and the way old chemical bonds are broken and new ones are made in the course of a reaction. When we classify reactions by their mechanisms, our attention is attracted above all by the way a covalent bond in a reacting molecule is cleaved. There are two such ways: homolytic and heterolytic.

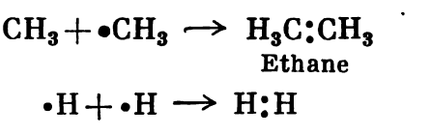
The *homolytic (radical) cleavage of the covalent bond* consists in the splitting of the bonding electron pair, and each of the *free radi-*

cals formed keeps one *unpaired electron*, remaining an electroneutral particle:



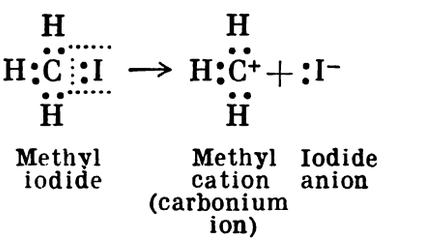
Nonpolar or low-polar bonds (C—C, N—N, C—H) usually undergo a radical cleavage at high temperature under the action of ultraviolet light or radioactive radiation.

The radicals and free atoms formed in the homolytic cleavage of a bond are unstable and can exist only for a very short time. These reactive intermediate particles undergo further transformations, passing into stable products. For example, the methyl radical and the hydrogen atom can be stabilized by *dimerization*:



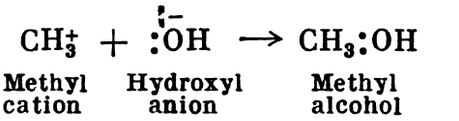
If a reaction mixture has other substances (impurities or reagents which are specially added), the radicals may be stabilized in other ways, which we will discuss later.

The *heterolytic* (*ionic*) *cleavage of the covalent bond* causes the formation of charged fragments: cations and anions. The bonding electron pair is not split, but wholly passes to one of the atoms (a more electronegative atom), which becomes negatively charged and turns into an anion. The second particle, which loses the electron, becomes positively charged and turns into a cation. Particles having a positive charge on the carbon atom are called *carbonium ions*.



Highly polar and readily polarizable bonds tend to undergo the heterolytic cleavage, which is promoted by solvents having a high dielectric constant and great polarity.

Carbonium ions, like free radicals, are unstable. They readily react with particles, which possess excess electron density in the form of a full or partial negative charge, and also with free electron pairs. Such particles are called *nucleophilic* ("nucleus loving"), e.g.,



Nucleophilic reagents are water, alkalies, ammonia and acid residues (e.g., ^-CN and $^-SO_3H$).

The heterolytic cleavage of the covalent bond in some cases can cause also the formation of organic anions (*carbanions*), e.g.,

$$CH_3{:}Li \longrightarrow :\bar{C}H_3 + Li^+$$

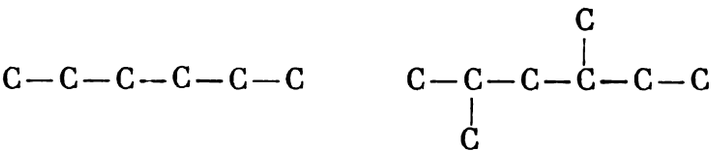
Carbanions are stabilized as a result of their reactions with *electrophilic* ("electron loving") reagents. They include the proton, metal cations, carbonium ions and organic residues having a partial positive charge. An example is the reaction of methyllithium with water:

$$CH_3{-}Li + \overset{\delta+}{H}{-}\overset{\delta-}{O}H \longrightarrow CH_4 + Li^+ + HO^-$$

Free radicals, carbonium ions and carbanions act as intermediate reactive particles in many organic reactions.

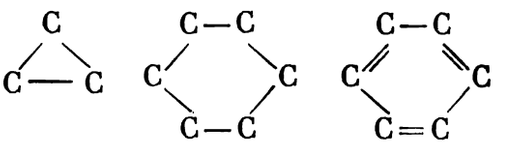
1.11. Classification of Organic Compounds. Any organic compound is based on the sequence of the chemically linked carbon atoms, i.e., on its *carbon skeleton*, which is of the following types:

(a) acyclic skeleton, i.e., unbranched (normal) (I) and branched (II) carbon chains:



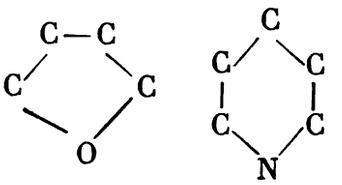
I II

(b) cyclic skeleton (III-V):



III IV V

(c) heterocyclic skeleton (VI and VII)



VI VII

All these formulas show the order of the chemical bond of atoms, but they do not give their spatial arrangement. For example, the unbranched carbon chain is in fact zig-zag and can be twisted spatially in the most fantastic manner.

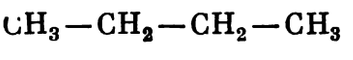
Organic compounds having carbon chains of types I and II are known as *fatty compounds*, or as *acyclic* or *aliphatic compounds*.

Compounds having carbon cycles represented by formulas III and IV are known as *alicyclic ones*. Formula V shows the carbon skeleton of benzene, which is the most important representative of the *aromatic compounds*. Formulas VI and VII show that the *heterocyclic ring* has atoms not only of carbon, but also of other elements, i.e., heteroatoms (from the Greek "heteros", meaning "different"). In this case, the name "carbon skeleton" itself becomes nominal, because the skeleton has atoms other than carbon.

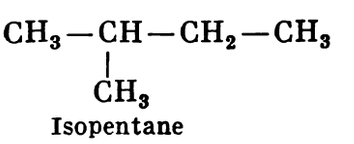
Compounds in which only hydrogen atoms are added to the carbon skeleton at the expense of the remaining carbon valencies are known as *hydrocarbons*.

Compounds which have only single carbon-carbon bonds are known as *saturated* ones, and those which have multiple carbon-carbon bonds, as *unsaturated* ones.

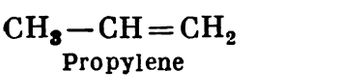
Several examples of the structural formulas of hydrocarbons and heterocyclic nuclei of different classes are given below:



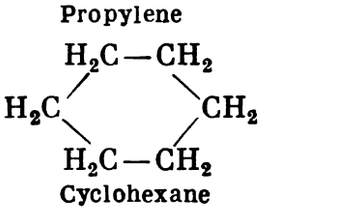
Butane — Saturated aliphatic hydrocarbon with an unbranched chain



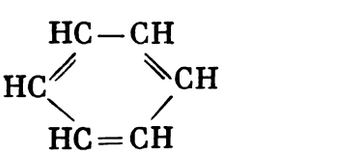
Isopentane — Saturated aliphatic hydrocarbon with a branched chain



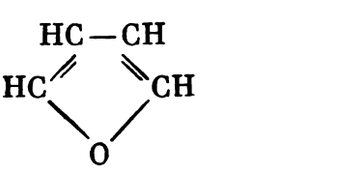
Propylene — Unsaturated aliphatic hydrocarbon



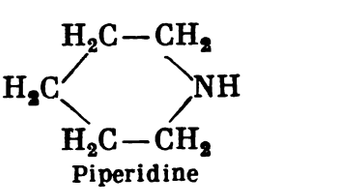
Cyclohexane — Saturated alicyclic hydrocarbon



Benzene — Simplest aromatic hydrocarbon



Furane — Oxygen-containing heterocycle



Piperidine — Nitrogen-containing heterocycle

Most organic molecules contain, besides carbon and hydrogen, atoms of other elements. It is precisely on these atoms that the chemical properties of organic substances depend above all. These atoms (oxygen, nitrogen, sulphur, etc.) belong to special groupings, known as *functional* (or characteristic) *groups*. The presence of a definite functional group determines the *class* to which organic compounds belong. The main functional groups and the classes of organic compounds which correspond to them are given in Table 1.3.

TABLE 1.3. **Functional Groups and Classes of Organic Compounds**

Functional groups	Class of compounds	Typical representatives	
		name	formula
Halogens F, Cl, Br, I	Halides	Methyl iodide	$CH_3—I$
Hydroxyl —OH	Alcohols	Methyl alcohol	$CH_3—OH$
	Phenols	Phenol	$C_6H_5—OH$
Carbonyl	Aldehydes	Acetaldehyde	$CH_3—C(=O)H$
$>C=O$	Ketones	Acetone	$CH_3—C(=O)—CH_3$
Carboxyl $—C(=O)OH$	Carboxylic acids	Acetic acid	$CH_3—C(=O)OH$
Nitro group $—NO_2$	Nitro compounds	Nitrobenzene	$C_6H_5—NO_2$
Amino group $—NH_2$	Amines	Ethylamine	$C_2H_5—NH_2$
Diazo group $—N_2X$	Diazo compounds	Benzenediazonium chloride	$C_6H_5—N_2Cl$
Mercapto group —SH	Thiols (mercaptans, thioalcohols)	Methyl mercaptan (methanethiol)	$CH_3—SH$
Sulpho group $—SO_3H$	Sulphonic acids	Benzenesulphonic acid	$C_6H_5—SO_3H$

C. Schorlemmer said as early as the last century that "organic chemistry is the chemistry of hydrocarbons and their derivatives"; by derivatives, he meant substances which are obtained by introducing functional groups into hydrocarbon molecules.

Heteroatoms which are in the composition of functional groups make it possible to subdivide the groups into *oxygen functions* OH, CO, COOH, etc.; *nitrogen functions* NO, NO_2, NH_2 and many others; *sulphur functions* SH, SO, SO_2, SO_3H, etc.; *phosphorus functions* PH_2, $PO(OH)_2$, etc.

The total number of the functional groups now known is very great, and only a part of them is considered even in voluminous textbooks of organic chemistry.

A molecule of an organic compound can have several functional groups. If these groups are the same (two halogens, two or three hydroxyls, etc.), such a compound is called *polyfunctional*. Organic compounds characterized by the presence of several *different* functional groups in a molecule are called *heterofunctional*.

Examples of mono-, poly- and heterofunctional organic compounds are given below:

$CH_3—CH_2—OH$ Ethyl alcohol	Monofunctional hydroxyl compound
$HOCH_2—CH(OH)—CH_2OH$ Glycerol	Polyfunctional hydroxyl compound
$H_2N—CH_2—COOH$ Glycine	Heterofunctional compound (amino acid)
$CH_3—CO—CH_2—COOH$ Acetoacetic acid	Heterofunctional compound (keto acid)

PART I

HYDROCARBONS

Hydrocarbons are organic compounds whose molecules contain atoms of only two elements: carbon and hydrogen. Hydrocarbons can differ from one another by the structure of the carbon skeleton. A large number of hydrocarbons can exist, because carbon atoms are able to form chains and cycles of different sizes and shapes, and various types of bonds. Hydrocarbons of various types differ from one another also by the degree of hydrogen saturation. The number of hydrogen atoms in a molecule of any hydrocarbon is *even*.

Chapter 2

ALKANES

Alkanes are hydrocarbons richest in hydrogen; they are maximally saturated with it. Hence the name *saturated* hydrocarbons. They are also called *paraffins*.

2.1. Homologous Series of Alkanes. Structure. Isomerism. Homologous series. The simplest member of alkanes is methane CH_4. There are several hydrocarbons similar to methane:

CH_4	Methane	C_9H_{20}	Nonane
C_2H_6	Ethane	$C_{10}H_{22}$	Decane
C_3H_8	Propane	$C_{11}H_{24}$	Undecane
C_4H_{10}	Butane	$C_{12}H_{26}$	Dodecane
C_5H_{12}	Pentane	$C_{13}H^{28}$	Tridecane
C_6H_{14}	Hexane	$C_{14}H_{30}$	Tetradecane
C_7H_{16}	Heptane	$C_{15}H_{32}$	Pentadecane, etc.
C_8H_{18}	Octane		

In this case, each member differs from the one before or after it by one CH_2 group. We can also derive a general formula for the series, C_nH_{2n+2}. We will learn later that all paraffins have similar chemical properties.

The series of compounds which have a similar chemical structure and similar properties, and which differ from one another in compo-

sition by CH_2— groups (methylene groups), is known as the *homologous series*. The members of this series are referred to as *homologues*, and the difference in the composition of two neighbouring members of the series, the group CH_2, is known as the *homologous difference*.

This series of compounds is called the homologous series of saturated hydrocarbons, paraffins or alkanes. It is sometimes also called by the first member of the series, i.e., the homologous series of methane.

The homologous series are a common phenomenon for organic chemistry as a whole. They are a brilliant example of the manifestation of one of the basic laws of nature: the law of the conversion of quantity into quality. Engels wrote in his *Dialectics of Nature* (Moscow, Progress Publishers, pp. 65, 66): "... by each addition of CH_2 a body is formed that is qualitatively distinct from the preceding one. ... Chemistry can be termed the science of the qualitative changes of bodies as a result of changed quantitative composition."

The discovery of the homology phenomenon has facilitated the investigation of organic substances: it is enough to study the properties of a typical representative of a series in order to have an understanding of the properties of the series as a whole.

The presence of structural isomerism limits the significance of the concept of "homologous series", because a true homologous series is formed only by unbranched compounds. The first member of the series is usually not typical of the series as a whole.

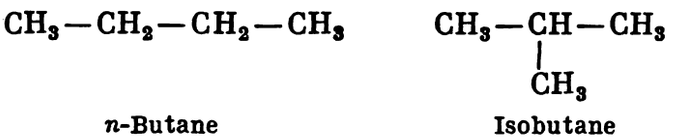
Structure. The structure of saturated compounds is characterized by a *single* bond between carbon atoms. *One electron pair* is used to form this bond, and electron orbitals overlap to the greatest extent on the straight line connecting the atomic nuclei. Such a bond is also known as the σ (sigma)-bond, while the electrons forming it, the σ-electrons. The distribution of the electron density of the σ-bond is symmetrical with respect to the axis which passes through the centres of the bonded atoms.

In saturated hydrocarbon molecules, carbon atoms are in the state of sp^3 hybridization, and each of them forms *four* σ-bonds with carbon or hydrogen. The state of sp^3 hybridization is characterized by the tetrahedral configuration of the carbon atom, i.e., the spatial direction of the bonds in alkane molecules is at an angle of 109°28′ (see Fig. 1.9). Numerical data on the lengths and energies of the bonds C—C and C—H are given in Table 1.2.

Isomerism. As we have already seen, isomerism is expressed in the existence of different substances which have the same molecular composition. Isomers originate most frequently owing to the differences in the chemical structure. When the order of the bond of atoms is different, their properties will also be somewhat different, because atoms linked directly exert the strongest influence on one

another. A change in the properties of individual atoms and bonds is exhibited in a change in the properties of a compound as a whole.

For example, the hydrocarbon of the C_4H_{10} composition is known to have two isomers: normal butane, a compound having an unbranched carbon chain, and isobutane, which has a branched carbon chain:

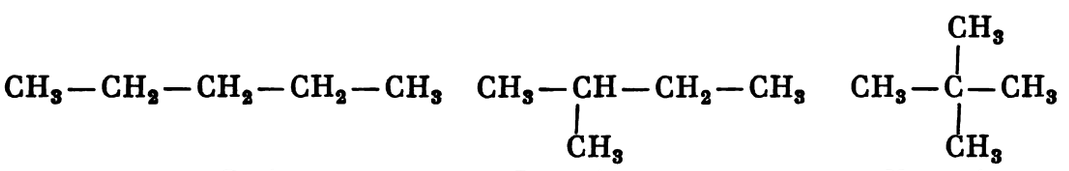


n-Butane Isobutane

Both hydrocarbons are gases, but they have a different boiling point: —0.5°C for butane and —11.7°C for isobutane. Isobutane was synthesized for the first time by Butlerov (1867), who thus proved that isomerism exists in hydrocarbons.

This type of isomerism, when substances are distinguished by a different order of the bond of atoms in a molecule, is known as *structural isomerism*. The isomerism of saturated hydrocarbons is engendered by the simplest type of structural isomerism: the *isomerism of the carbon skeleton*. Compounds which have an unbranched carbon chain are called *normal compounds*.

The first members of the homologous series of paraffins, i.e., methane, ethane and propane, exist only in one form; they do not have isomers. As we have already seen, butane has two isomers. The hydrocarbon C_5H_{12} (pentane) is known to have three isomers:



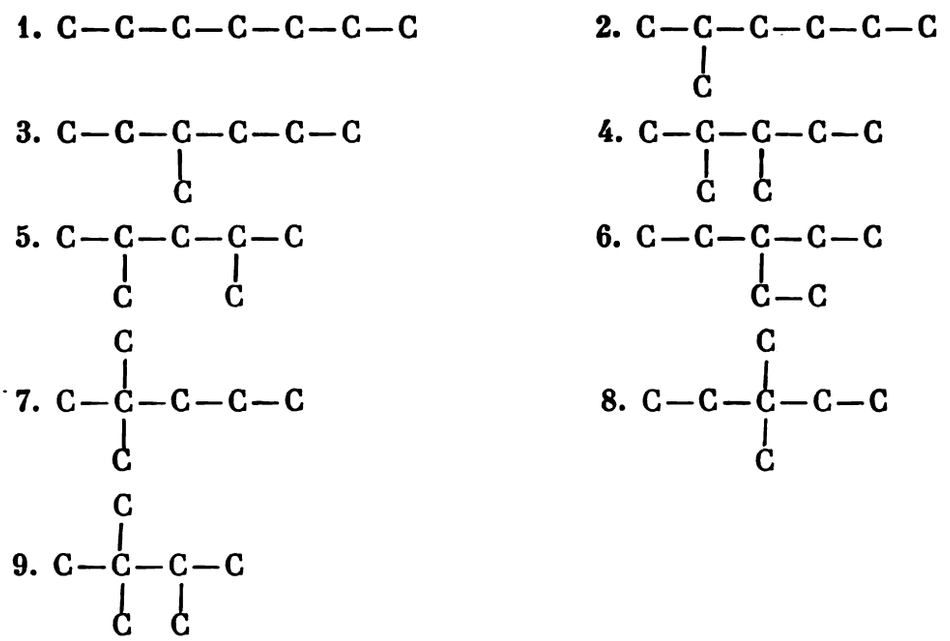
n-Pentane Isopentane Neopentane

The number of theoretically possible isomers grows as that of carbon atoms in a molecule increases. For example, it is 5 for hexane, 9 for heptane, 18 for octane, 35 for nonane, 4347 for pentadecane ($C_{15}H_{32}$), and 4,111,846,763, or over four billion, for triacontane ($C_{30}H_{62}$).

This does not mean that all the theoretically possible isomers are really known. They have been obtained for the hydrocarbons C_1—C_9, but only some of the higher members of the series are known.

In deriving formulas for isomers, it is expedient to preliminarily plot structures of carbon skeletons, gradually shortening the main chain and arranging the carbon atoms, removed from this chain, in the form of branches (side chains) in all possible positions. Let us consider, for example, the structures of a carbon skeleton of

isomeric heptanes (C_7):



Complete formulas for hydrocarbons are obtained after supplementing the structures of carbon skeletons with the necessary number of hydrogen atoms.

As the foregoing examples show, carbon atoms in saturated hydrocarbons are not equivalent: they may be combined with a different number of atoms of carbon and hydrogen.

If a carbon atom uses one unit of valence for a carbon-carbon bond, it is known as a *primary* carbon atom; if two, a *secondary* one; if three, a *tertiary* one, and if four, a *quaternary* one. Molecules of normal alkanes have only primary (at the chain ends) and secondary (in the middle of a chain) carbon atoms.

Monovalent residues, obtained when a hydrogen atom is removed from alkanes, are known as *alkyl radicals* or *alkyls*. The names of alkyls are widely used in the nomenclature of organic compounds, i.e., when names of organic compounds are being composed. We will learn later that alkyls can exist for a short time as intermediate products of reactions (see Sec. 7.9).

The names of alkyls are derived from those of the appropriate hydrocarbons, the ending **ane** being replaced by **yl**. The alkyl series is given below:

CH_3	Methyl	C_4H_9	Butyl
C_2H_5	Ethyl	C_5H_{11}	Pentyl (amyl)
C_3H_7	Propyl	C_6H_{13}	Hexyl

The general formula for alkyls is C_nH_{2n+1}, and they are often denoted by the letters Alk or R for the sake of brevity in the formu-

las of organic compounds. Each of the molecules of methane and ethane forms one monovalent radical (methyl, ethyl). A hydrogen atom can be eliminated from a molecule of propane $CH_3—CH_2—CH_3$ in two ways: it can be eliminated from the primary carbon atom with the formation of the propyl radical $CH_3—CH_2—CH_2—$ and from the secondary carbon atom, when the secondary propyl radical, or isopropyl, $CH_3—\underset{|}{CH}—CH_3$ is formed. Each of the molecules of butane and isobutane can also form two monovalent radicals:

$CH_3—CH_2—CH_2—CH_2—$ Butyl

$CH_3—\underset{|}{CH}—CH_3$ Secondary butyl (*sec*-butyl)

$CH_3—\underset{|}{CH}—CH_2—$ Isobutyl

$CH_3—\underset{|}{\overset{|}{C}}—CH_3$ Tertiary butyl (*tert*-butyl)

These examples show that alkyls can be *primary*, *secondary* and *tertiary*, depending on whether the primary, secondary or tertiary carbon atom has free valence.

2.2. Conformations. Molecular Models. Structural formulas on a plane show the order of the chemical bond of atoms in a molecule, but not their three-dimensional arrangement.

In our consideration of the valence state of the carbon atom, we have become acquainted with the data on the spatial direction of valence bonds and the sizes of the angles between them.

Let us consider a model of the ethane molecule more carefully. The changing of the spatial position of one methyl group relative to another by its rotation around the C—C bond does not disturb the order of the chemical bond (chemical structure) or bond angles and bond lengths. In this case, the ethane molecule can assume different geometric shapes, which are characterized by the mutual rotation of methyl groups. Two of these shapes are illustrated perspectively in Fig. 2.1.

These shapes can be represented more vividly as projections (Fig. 2.2) obtained when they are examined down the C—C bond. Such a technique of representation is known as Newman formulas (projections). The front carbon atom, being the closest to the observer, is in the centre of the formula, and three bonds go from it to hydrogen atoms. The bonds of the second carbon atom, which is away from the observer, "peep" from round the circle, as it were.

As we can see in Fig. 2.2, the mutual arrangement of methyl groups in this model can be characterized by angle φ. If we suppose

that a definite stereoisomer, which differs from others, corresponds to every value of angle φ, the indisputable fact that only ethane, without isomers, exists is contradicted. Therefore, van't Hoff introduced the concept of the free rotation of groups around single bonds, i.e., the concept that there are no special shapes of molecules having a definite value of angle φ. This concept of van't Hoff's was specified later. It turned out that the arrangement characterized by angle φ^0 (see Fig. 2.2*b*), the so-called *eclipsed* arrangement, is less advantageous energetically than the arrangement having angle φ'

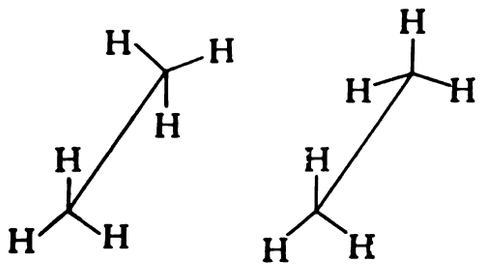


Fig. 2.1. Perspective formulas of two ethane conformations

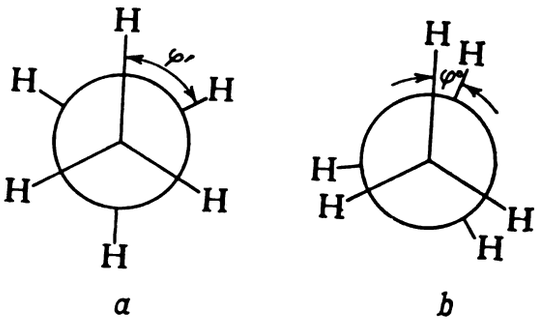


Fig. 2.2. Newman's formulas of two ethane conformations:
a—staggered; *b*—eclipsed

(Fig. 2.2*a*), or the *staggered* arrangement. Thus, van't Hoff's postulate of the free rotation of groups around single bonds was replaced by the concept that, as a result of rotation around single bonds, a molecule tends to assume a geometric shape which is the most advantageous and has the least energy.

Different geometric shapes of molecules that can be converted into one another by rotation about single bonds are called *conformations* or *rotational isomers* (*rotamers* or *conformers*).

In rotation around the σ-bond, the distances between nonbonded atoms change; the degree of repulsion between them grows, and potential energy increases, as the distance decreases.

In the eclipsed conformation, the distances between hydrogen atoms in the ethane molecule are minimum, while in the staggered conformation, they are maximum, and therefore the potential energy of repulsion will be greater in the eclipsed conformation. But the difference in energies is only 12 kJ/mole; thus, the transition from one conformation to another occurs readily, and they cannot be separated as stable isomers.

A large number of conformations are possible for molecules of greater complexity, and those which are energetically more advantageous are realized first of all. A long carbon chain can assume the most diverse geometric arrangements as it twists. Several conformations for a chain of five carbon atoms are shown in Fig. 2.3.

The planar shapes represented in the figure (zig-zag *a*, claw-shaped *b* and irregular *c*) are only a part of the total number of possible conformations: carbon atoms do not by any means have to be on the same plane. Regardless of the conformation assumed by a chain of carbon atoms which are linked by single bonds, three of its neighbouring atoms will never be on one straight line.

The larger part of organic substances is a mixture of conformers which are in equilibrium. Among the latter, the most advantageous

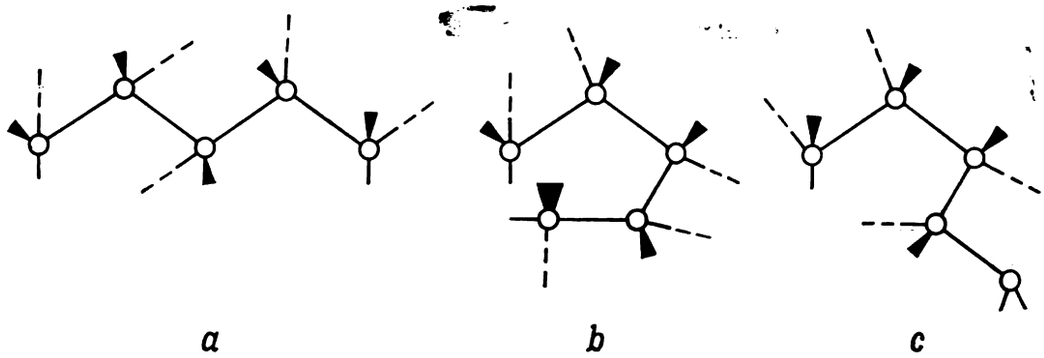


Fig. 2.3. Conformations of a chain consisting of five carbon atoms:
a—zig-zag; *b*—claw-shaped; *c*—irregular

ones, i.e., those which have minimum internal energy, predominate. Many physical and chemical properties of substances depend on the actual conformation.

X-ray investigations of alkanes of a normal structure in a solid state show that they have a regular zig-zag conformation.

The simplest models, like those represented in Fig. 1.14, show the order of the bond of atoms in a molecule and the quantity of the bond angle, but they do not give a correct idea of the size of atoms, interatomic distances and intramolecular space filling. But, in fact, there are no voids in molecules. A correct idea of the molecular structure and of intramolecular space filling can be obtained by space-filling models, which are known also as the Stuart-Briegleb models. The basis for constructing molecular models is the three-dimensional arrangement of σ-bonds. In preparing the models, it is taken into account that every atom is characterized by two "radii": the intermolecular or the van der Waals radius *a* and the atomic or covalent radius *r*.

The van der Waals radius characterizes the volume of the non-bonded atom and is equal to halfway distance of the nearest approach of two like atoms of two adjacent molecules. The size of the covalent radius depends on the nature of an element, its valence state and the bond order. The covalent radius is equal to half the distance between two same atoms linked by a covalent bond. The distance between the centres of the linked atoms characterizes the bond length.

If two atoms establish a chemical bond, their centres approach one another closer than is allowed by the van der Waals radii; in this case, the centres of the bonded atoms will be at a distance equal to the sum of their covalent radii. To show this, a segment equal to the covalent radius (on a definite scale) is plotted on a model from the centre of the sphere (atom) at a definite bond angle, and spherical segments are cut off on this distance perpendicular to the

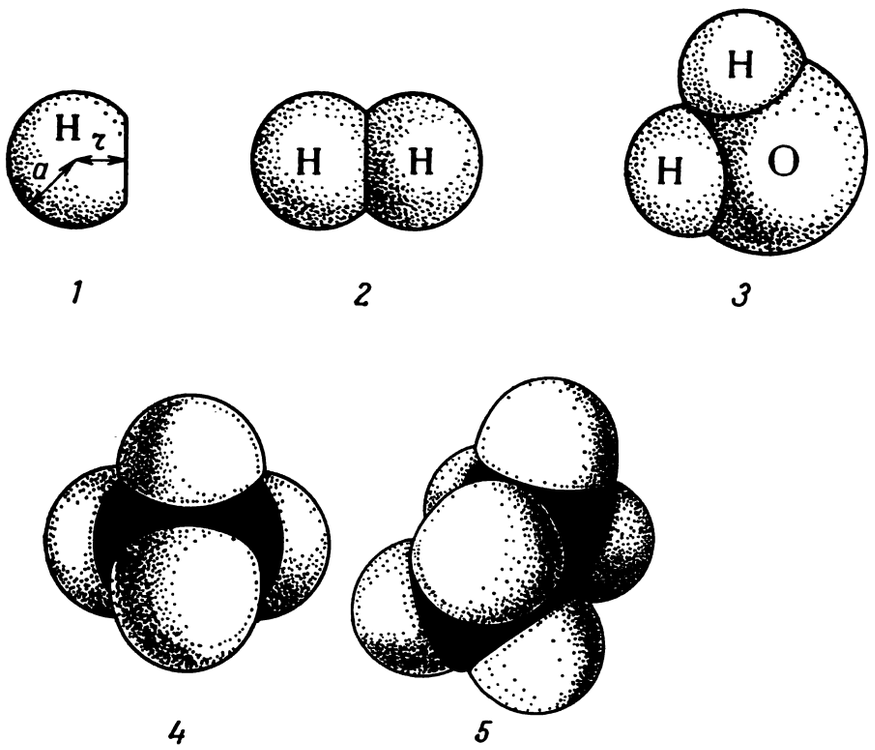


Fig. 2.4. Space-filling models of molecules:
1—hydrogen atom (*a*—van der Waals radius, *r*—covalent radius); *2*—hydrogen molecule; *3*—water; *4*—methane; *5*—ethane

direction of the bond angle. The atom of a monovalent element, say hydrogen, is represented by a sphere with one section (Fig. 2.4.*1*). Putting together two such models by their cut-off parts, we obtain a model of the hydrogen molecule (Fig. 2.4.*2*). It correctly shows the interatomic distance and limits the region into which some other atom cannot penetrate. The model of the bivalent oxygen atom is a sphere having two sections arranged at an angle of about 105°. A model of the water molecule can be built from a model of the oxygen atom and two models of the hydrogen atoms (Fig. 2.4.*3*). The model of the carbon atom in the state of sp^3 hybridization is a sphere having four sections at tetrahedral angles. In applying the models of hydrogen atoms to the sections, we obtain a model of the methane molecule (Fig. 2.4.*4*), and so forth.

2.3. Nomenclature of Alkanes. Nomenclature defines the rules of composing the names of compounds. The name of an organic compound should reflect not only the composition, but also the structure of its molecule. In other words, the name should allow us to easily and correctly write a structural formula.

The so-called *"rational" nomenclature* began to develop from the middle of the nineteenth century; according to it, organic substances were the products of the growing complexity of the simplest representative of a given homologous series. This nomenclature is readily used even today for simple compounds.

In 1892, the rules of a new scientific nomenclature were approved at the International Chemical Congress in Geneva; it became known as the "Geneva nomenclature". The rules of the nomenclature for open-chain compounds were worked out in especially great detail. The name of any organic substance in the Geneva nomenclature is based on the name of the hydrocarbon from which a given compound can be obtained by substitution. This nomenclature is called *substitutive.*

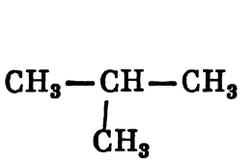
In 1930, new rules on the nomenclature of organic compounds were adopted in Liège (Belgium); they became known as the "Liège rules". Work on nomenclature continued, and now the most complete are the rules of the Commission on Nomenclature of Organic Compounds of the International Union of Pure and Applied Chemistry (abbreviated as the IUPAC rules from the initial letters of the name of the union).

The IUPAC rules generalize the experience gained in nomenclature down the century and are the modern international rules of organic compound nomenclature that have hundreds of sections. By the IUPAC rules, both rational (radicofunctional) and substitutive names can be used. We will become gradually acquainted with modern nomenclature as the need for this arises. Let us begin by familiarizing ourselves with the names of paraffins.

The first four representatives of the alkane series have casual *trivial names* (from the Latin "trivialis", meaning "ordinary"): methane, ethane, propane and butane. The names of the subsequent members of the series are derived from the Greek numerals, which indicate the number of carbon atoms in a molecule; the ending *ane*, common to the entire homologous series, is added to them. These names apply to both unbranched and branched isomers, but the latter then lose their unequivocal nature: such names do not show the isomeric structure. To denote isomers, trivial names are prefixed with *iso-*, *neo-*, etc.

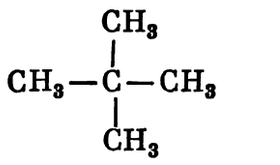
In *rational nomenclature* the names of all the alkanes are formed from the name of the simplest member of the homologous series, methane, to which the designation of hydrocarbon radicals substituting hydrogen atoms in them is added. The names end with the

word "methane", while the radicals are enumerated in the order of growing complexity. If there are several same radicals, their number is indicated by means of prefixes, i.e. by the numerals di- (two), tri- (three), tetra- (four). Here are examples in which rational names are given together with some trivial ones in parentheses:



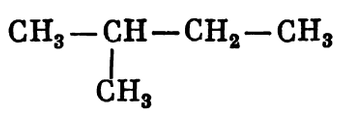
I

Trimethylmethane (isobutane)



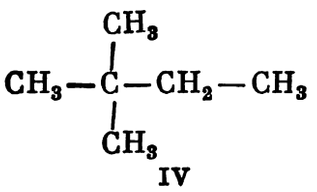
II

Tetramethylmethane (neopentane)



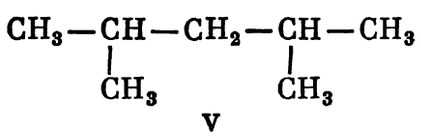
III

Dimethylethylmethane



IV

Trimethylethylmethane (neohexane)



V

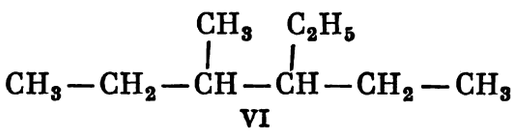
Dimethylisobutylmethane

In composing a name according to *substitutive nomenclature*, hydrocarbons having a branched chain are regarded as derivatives of normal alkanes, whose chains have hydrocarbon radicals instead of hydrogen atoms. The principal (or main) chain is of maximum length, and the carbon atoms in it are numerated from the end which is the closest to the branching. In the name of a compound, the figure indicates the number of the carbon atom to which the substituting radical is attached, and then the name of the radical and that of the principal chain are given. If the radicals are repeated, the figures indicating their position are enumerated, while the number of the same radicals is indicated by the prefixes di-, tri-, tetra-. The name of a hydrocarbon thus has the following form:

Figures—alkyls—principal chain—suffix *ane*

According to modern nomenclature, the foregoing structures I-V should be called: compound I—2-methylpropane; II—2,2-dimethylpropane; III—2-methylbutane; IV—2,2-dimethylbutane, and V—2,4-dimethylpentane.

For compound VI, the beginning of numeration is determined by a more simple methyl radical:

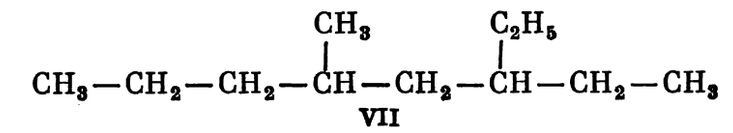


VI

3-Methyl-4-ethylhexane

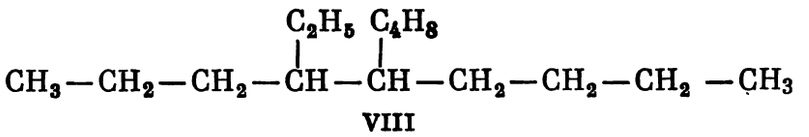
For compounds VII and VIII, the beginning of numeration is determined by the ethyl radical: in structure VII, it is the closest

one to the chain end, and in structure VIII, it is the simplest one among two equidistant ones from the end of the principal chain. According to the IUPAC rules, radicals can be numbered and enumerated also in alphabetical order (names in parentheses):



VII

5-Methyl-3-ethyloctane
(3-ethyl-5-methyloctane)

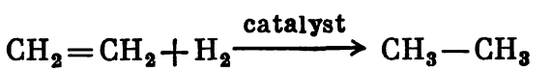


VIII

4-Ethyl-5-butylnonane
(4-butyl-5-ethylnonane)

2.4. Preparation of Alkanes. Various methods of obtaining alkanes can be divided into three groups.

Reactions which are not accompanied by a change in the number of carbon atoms in a molecule. Such reactions include, for example, the hydrogenation of unsaturated hydrocarbons. Transformation consists in the addition of hydrogen to multiple bonds in the presence of catalysts (nickel, platinum):

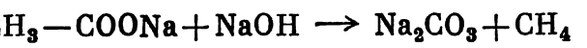


We will become acquainted with this reaction in greater detail later (see Sec. 4.3).

Reactions accompanied by a decrease in the number of carbon atoms in a molecule. They are:

(a) Cracking (see Sec. 2.6).

(b) Fusion of monobasic carboxylic salts with alkalies:



Reactions accompanied by the growing complexity of the carbon skeleton.

(a) Wurtz reaction (1855), i.e., the action of metallic sodium on alkyl halides:

The reaction can be used above all for preparing hydrocarbons whose molecules consist of two identical halves. To obtain hydrocarbons of unsymmetrical structure, a mixture of two alkyl halides should be taken, but then three reaction products are obtained

instead of one:

$$CH_3I + C_2H_5I \xrightarrow{2Na} \begin{cases} \longrightarrow CH_3-CH_3 \text{ (Ethane)} \\ \longrightarrow CH_3-C_2H_5 \text{ (Propane)} \\ \longrightarrow C_2H_5-C_2H_5 \text{ (Butane)} \end{cases}$$

(b) Direct synthesis from elements. Methane is formed in an electric arc between carbon electrodes in the presence of hydrogen:

$$C + 2H_2 \longrightarrow CH_4$$

Such a type of reactions carried out under different conditions became practically important in coal hydrogenation (Bergius, 1920). To this end, a suspension of pit coal in heavy petroleum oils is heated with hydrogen at a pressure of the order of 300 kg/cm^2 in the presence of iron and manganese catalysts at about 400°C. A mixture of hydrocarbons, gasoline, is then obtained.

(c) Catalytic hydrogenation of carbon monoxide over iron, cobalt and nickel at 200-400°C causes the formation of liquid hydrocarbons, which are used as gasoline:

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

2.5. General Characteristics of the Physical and Chemical Properties of Alkanes. Physical properties. Table 2.1 shows that the

TABLE 2.1. **Physical Properties of Some Normal Alkanes**

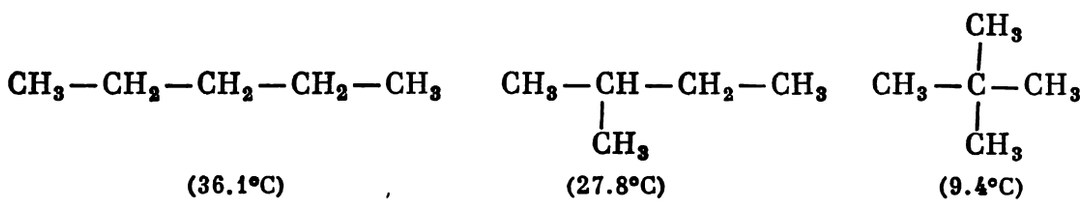
Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Methane	CH_4	—182.5	—161.5	0.424 [a]
Ethane	C_2H_6	—183.7	—88.6	0.546 [a]
Propane	C_3H_8	—187.6	—42.2	0.585 [a]
Butane	C_4H_{10}	—138.3	—0.5	0.579 [b]
Pentane	C_5H_{12}	—129.7	+36.1	0.626
Hexane	C_6H_{14}	—95.3	68.8	0.659
Heptane	C_7H_{16}	—90.6	98.4	0.684
Decane	$C_{10}H_{22}$	—30.0	173.0	0.730
Tetradecane	$C_{14}H_{30}$	+5.5	253.0	0.764
Pentadecane	$C_{15}H_{32}$	10.0	270.5	0.769
Hexadecane	$C_{16}H_{34}$	18.1	287.5	0.775 [c]
Eicosane	$C_{20}H_{42}$	36.5	344.0	0.778 [c]
Pentacontane	$C_{50}H_{102}$	93.0	421.0 (at 15 mm Hg)	0.942 [c]
Hectane	$C_{100}H_{202}$	115.4	—	—

Note: *a* – at boiling point; *b* – under pressure; *c* — at melting point.

first four members of the homologous series of alkanes under ordinary conditions are gaseous substances, the compounds from C_5

to C_{15} are liquids, and those from C_{16} onwards are solids. In the homologous series of alkanes, the boiling and melting points, and relative density, gradually increase. This makes it possible to predetermine the properties of an unknown member of the series on the basis of the properties of its neighbours. For example, the boiling point of hexane is 68.8°C, and that of heptane, 98.4°C. The difference in composition by one CH_2 group leads to an elevation of the boiling point by 29.6°C (homologous difference in the boiling points). Proceeding from this, the boiling point of octane can be calculated; 98.4°C + 29.6°C = 128°C. It differs from the point found experimentally by approximately 2°C. In this calculation, it should be taken into account that the homologous difference in the boiling points (like the influence of homology on all the other physical constants) does not remain unchanged: for the higher members of the series, a change in composition by a CH_2 group affects the properties of a molecule to a relatively smaller extent. Alkanes with a branched chain have a lower boiling point than isomers with a normal chain.

The boiling points of isomeric pentanes are given as an example:



In nonpolar liquids, van der Waals forces act between molecular surfaces. The larger a molecule and its surface, the greater is intermolecular interaction. The boiling points rise as the relative molecular mass increases. A branched molecule tends to become spherical, its surface area and intermolecular forces diminish, and the latter are overcome more readily at lower temperatures.

Conversely, the melting points rise as the carbon chain becomes more branched. The density of all the alkanes is less than unity. They are practically water-insoluble, but are soluble in ether and other organic solvents. Methane and ethane have almost no odour, the hydrocarbons C_3-C_{15} have the well-known odour of gasoline or kerosene, and the higher members of the series have no odour owing to their low volatility.

Chemical properties. Alkanes are poorly active chemically, and therefore they were called paraffins (from the Latin "parum affinis", meaning "too little affinity"). The famous Russian chemist M. I. Konovalov (1858-1906) figuratively called paraffins "chemical corpses" for their passivity.

The chemical behaviour of saturated hydrocarbons is determined by the nature and strength of the bonds in their molecules. The carbon-carbon (C—C) bond is stable owing to the small size of the

carbon atom and its tetrahedral configuration in the state of sp^3 hybridization, and this is conducive to the maximum concentration of the electronic charge between nuclei. The carbon-hydrogen (C—H) bond is strong, because, when it is being formed, the sp^3 orbital of carbon comes close to the nucleus of the hydrogen atom, since, unlike the atoms of other elements, the hydrogen atom does not have "inner" electrons which could repulse the electronic charge of the carbon atom. In alkaline molecules, the σ-bond is poorly polarized, because the electronegativities of carbon and hydrogen scarcely differ in their values (2.5 and 2.1, respectively). Therefore, saturated hydrocarbons are low polar and poorly polarizable. They do not tend to undergo heterolytic cleavage. Attacks by nucleophilic and electrophilic reagents are hindered, and therefore paraffins are stable with respect to ionic reagents. They are unaffected by concentrated acids (nitric, sulphuric and other acids), fused and concentrated alkalies, and ordinary oxidizing agents (potassium permanganate, chromic-acid mixture). Metals, even alkali metals, do not force out hydrogen from these compounds. These properties are used in practice, e.g., alkali metals are kept in kerosene, various metallic articles are coated with lubricants to protect them from corrosion, concentrated sulphuric acid and concentrated alkalies are used for purifying oil products, and so forth.

Only a homolytic, radical cleavage of bonds is possible for saturated hydrocarbons; in this case, hydrogen atoms are substituted, the carbon skeleton is split up (cracking), and partial or complete oxidation (combustion) occurs. All this determines the range of reactions which paraffins can undergo, including especially radical reactions of substitution, which occur under rather rigid conditions (the action of light, high temperature, etc.). *Alkanes are incapable of undergoing addition reactions*, and this fundamentally distinguishes them from unsaturated hydrocarbons.

Although the C—H bond is stronger than the C—C bond (compare their energies and lengths; see table 1.2), reactions with the elimination of hydrogen occur more frequently, because the C—H bonds are arranged on the surface of an organic molecule and are therefore more susceptible to the action of reagents.

The mechanism of the replacement of hydrogen by chlorine and bromine in alkanes has been studied best of all. These reactions occur by the *radical chain mechanism*. The chain mechanism consists in the constant reproduction of active particles which are conducive to the conversion of new molecules of a reagent. Under ordinary conditions, molecular chlorine and bromine practically do not react with saturated hydrocarbons. Only in the atomic state are they capable of abstracting a hydrogen atom from the alkane molecule. Therefore, halogen molecules must be preliminarily broken down into free atoms, which initiate a chain reaction. This

can be effected under the action of light or temperature. For example, when methane is being chlorinated, the process occurs in the following way:

$$Cl_2 \xrightarrow{\text{light or heat}} 2Cl\cdot \qquad (2.1)$$

The chlorine atom then attacks the hydrogen atom (and not the carbon atom) in the methane molecule. Hydrogen splits away and a free methyl radical is formed:

$$H_3C{:}H + \cdot Cl \longrightarrow H{:}Cl + H_3C\cdot \qquad (2.2)$$

At the next stage, the methyl radical attacks the chlorine molecule; as a result, methyl chloride and the chlorine atom are formed:

$$H_3C\cdot + Cl{:}Cl \longrightarrow H_3C{:}Cl + Cl\cdot \qquad (2.3)$$

The chlorine atom attacks the next methane molecule, and so forth.

The reactions (2.2) and (2.3) characterize *chain growth*; they are repeated until the occurrence of the *chain termination*, i.e., the destruction of the free radical which leads the chain. In this case, chain termination can occur as a result of one of the following reactions:

$$2Cl\cdot \longrightarrow Cl_2 \qquad (2.4)$$

$$2H_3C\cdot \longrightarrow CH_3{-}CH_3 \qquad (2.5)$$

$$H_3C\cdot + Cl\cdot \longrightarrow CH_3{-}Cl \qquad (2.6)$$

and also as a result of the collision of radicals against the vessel walls.

The steps of initiation of a chain, its propagation and termination characterize all the chain reactions. An interesting feature is that they cannot begin without an "external impetus", i. e., the appearance of a free radical, which initiates the chain reaction. In this case, a very inconsiderable number of initiator radicals is enough to effect the chain transformation of considerably large amounts of a substance. Large concentrations of free radicals can even be harmful, because chain terminations according to the foregoing equations occur more frequently under these conditions.

Radical reactions are retarded by substances which readily react with free radicals (inhibitors). We are indebted very much to Academician N. N. Semyonov for the information on chain reactions that he gave in his works. He was awarded the Nobel Prize for his investigations in this field.

2.6. Alkane Reactions. Halogenation. Radical halogenation, whose mechanism has been considered in the previous section, is an important alkane reaction. As halogenating agents, not only chlorine, but also bromine can be used. Iodine is incapable of undergoing a reaction of direct hydrogen substitution, while fluorine acts too

energetically and, if special precautions are not taken, completely destroys organic molecules. In industry, alkanes are thermally chlorinated at temperatures of the order of 300°C.

All the atoms of hydrogen in methane can be successively subjected to radical substitution for chlorine. When the first substitution product, methyl chloride CH_3Cl, accumulates, it can be attacked by the chlorine atom and the free radical $\cdot CH_2Cl$ can be formed; when this radical reacts further with the chlorine atom $Cl\cdot$, it produces a disubstituted product: methylene chloride CH_2Cl_2. When chlorine is in excess, substitution will occur further with the formation of the compounds $CHCl_3$ and CCl_4. As a result, a mixture of halogen derivatives of methane is formed. The sequence of these reactions is schematically illustrated below:

$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HCl]{Cl_2} \underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} \xrightarrow[-HCl]{Cl_2} \underset{\substack{\text{Methylene}\\\text{chloride}}}{CH_2Cl_2} \xrightarrow[-HCl]{Cl_2} \underset{\text{Chloroform}}{CHCl_3} \xrightarrow[-HCl]{Cl_2} \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4}$$

In the schemes of organic reactions, unlike equations, coefficients are not given; reagents and reaction conditions are often written above the arrow, while by-products are omitted or written with a negative sign under the arrow. The schemes concentrate attention on what is of the greatest importance, and therefore they are often far more clear than equations. If the positive sign and the sign of equality between left and right members of an equation are used, it is necessary to observe all the rules in writing equations, selecting coefficients, and so forth.

Other alkanes, like methane, can also undergo chlorination. The main direction of entry of halogen is determined by the regularities which were first studied by V. V. Markovnikov: substitution occurs most readily at the tertiary carbon atom, then at the secondary one and, lastly, at the primary one; in the formation of polyhalogen substituted compounds, halogen atoms mainly replace hydrogen at the same carbon atom or at adjacent ones:

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[-HCl]{Cl_2} CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[-HCl]{Cl_2}$$

$$\longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[-HCl]{Cl_2} CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

These regularities are due to the fact that the bond energies of hydrogen with primary, secondary and tertiary carbon atoms are

unequal, constituting 415, 390 and 376 kJ/mole, respectively. Therefore, in halogenation, hydrogen attached to the tertiary carbon atom is substituted at a greater rate.

The selectivity of substitution depends on the nature of a halogen and the conditions under which a process is being carried out. At low temperature, the weakest bond C—H (for the tertiary carbon atom) is ruptured. Selectivity decreases as temperature rises. For example, the relative rate at which hydrogen abstracts from the groups CH_3, CH_2 and CH in chlorination in a gaseous phase at 100°C can be expressed by the ratio 1 : 4.3 : 7; in chlorination under the action of light, it is 1 : 3.8 : 5, and at 300°C, 1 : 3.3 : 4.4, i. e., selectivity diminishes. Selectivity is higher for bromine than for chlorine. For example, at 127°C, the relative rate of bromination of the same groups is expressed by the ratio 1 : 82 : 1600. When isopentane $(CH_3)_2CHCH_2CH_3$ is being brominated in the gaseous phase, the yield of the tertiary product is approximately 20 times greater than that of the secondary one.

In calculating the yield of different isomers, account should be taken of not only relative reactivity, but also the number of reacting (primary, secondary and tertiary) atoms. For example, in the chlorination of isopentane $(CH_3)_2CHCH_2CH_3$, the above-mentioned relative rate of hydrogen substitution should be multiplied by the number of H atoms of the corresponding type, i.e., for primary ones, $1 \times 9 = 9$; for secondary ones, $3.8 \times 2 = 7.6$, and for tertiary ones, $5.0 \times 1 = 5.0$. Taking this into account, we obtain about 42 per cent of primary chlorine derivatives (two isomers), 35 per cent of the secondary chlorine derivative (one isomer) and only 23 per cent of the tertiary one, notwithstanding the greater reactivity of the tertiary H atom.

Nitration. At ordinary temperature, paraffins are stable toward the action of concentrated nitric acid. But the nitration reaction, the substitution of hydrogen for the nitro group NO_2, occurs when they are heated with dilute nitric acid or nitrogen oxides.

This reaction was first effected by M. I. Konovalov in 1888 by heating paraffins with 10-percent nitric acid to 140°C under pressure. It is now known as *Konovalov's reaction*:

$$\underset{\text{Hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3} \xrightarrow{HONO_2} \underset{\text{2-Nitrohexane}}{CH_3-\overset{\overset{NO_2}{|}}{CH}-CH_2-CH_2-CH_2-CH_3}$$

The reaction will be considered in greater detail in the section on nitro compounds (Sec. 14.2).

Sulphochlorination. The radical reaction of sulphochlorination occurs when a mixture of sulphur dioxide and chlorine acts on paraffins. This radical process is initiated photochemically, i.e., by

ultraviolet light:

$$Cl_2 \xrightarrow{\text{light}} 2Cl\cdot$$
$$RH + Cl\cdot \longrightarrow R\cdot + HCl$$
$$R\cdot + SO_2 \longrightarrow RSO_2\cdot$$
$$RSO_2\cdot + Cl_2 \longrightarrow \underset{\text{Sulpho-chloride}}{RSO_2Cl} + Cl\cdot, \text{ etc.}$$

Sulphochlorides (acid chlorides of sulpho acids) are readily hydrolized to sulpho acids RSO_2OH, whose sodium salts RSO_2ONa are called *sulphonates*. Sulphonates with the number of carbon atoms in the C_{16}-C_{18} range are of practical importance as detergents (see Sec. 12.6).

Oxidation. As we have already seen, paraffins at room temperature are stable toward the action of atmospheric oxygen and ordinary oxidizing agents. When paraffins are ignited in the air, they inflame and burn, turning into carbon dioxide and water:

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Paraffins are oxidized along the chain mechanism. They are a valuable, highly calorific fuel; they have much hydrogen, whose calorific value is greater than that of carbon. The most important result of methane combustion is heat evolved in it:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 891 \text{ kJ/mole}$$

When one kilogram of methane burns up, 57,000 kJ are evolved. Combustion is one of the main paraffin reactions used in practice, and natural gas and petroleum are the most important sources of heat and energy.

When paraffins are oxidized by atmospheric oxygen under milder conditions, we obtain oxygen-containing organic substances: alcohols, aldehydes, ketones and acids. For example, acetic acid is produced in industry when butane is oxidized (see Sec. 12.5). The oxidation of higher alkanes for obtaining higher fatty acids (S. S. Nametkin's work) has become of great industrial importance.

Cracking. Heating up to 400-600°C communicates enough energy to paraffin molecules for the homolytic cleavage of carbon-carbon bonds. This process is known as *cracking*.

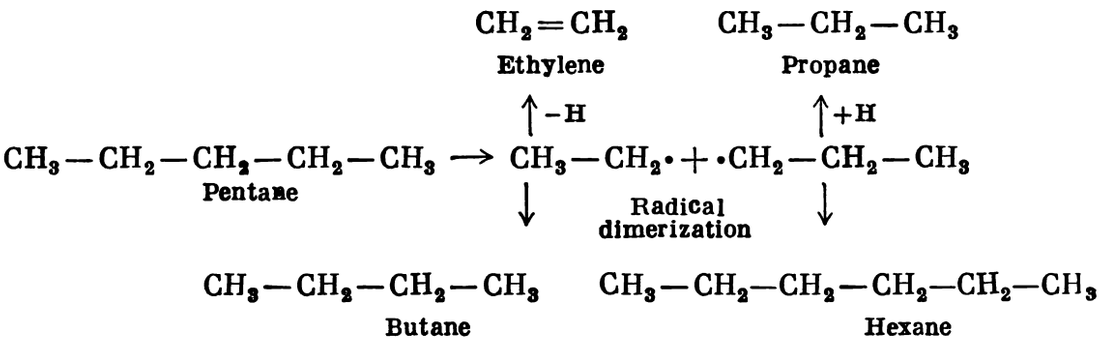
When saturated hydrocarbons are cracked, more simple saturated and unsaturated hydrocarbons are formed, e.g.,

$$\underset{\text{Butane}}{CH_3-CH_2-CH_2-CH_3} \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + \underset{\text{Ethylene}}{CH_2=CH_2}$$

This reaction is of great practical importance. Cracking is used to convert high-boiling oil fractions (mazut) into valuable low-boiling liquid products, such as gasoline and kerosene, and also

into the simplest hydrocarbon gases, which are raw material for industrial organic synthesis.

Cracking consists in the homolytic cleavage of carbon-carbon bonds under the action of high temperature or with the aid of catalysts. The radicals formed in this case are stabilized in various ways:



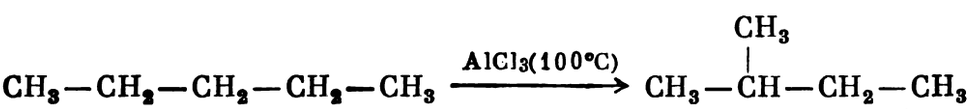
For details on the cracking mechanism, see Sec. 4.3.

Cracking conditions affect cracking results, i.e., they affect the ratio of liquid and gaseous products, the share of saturated and unsaturated hydrocarbons, and the "depth" of cracking (degree of decomposition of complex molecules). At higher temperatures (650-700°C), deeper decomposition occurs; this process is known as pyrolysis, in the course of which much hydrogen, coke, and the simplest saturated and unsaturated hydrocarbons are formed. Other processes occur together with cracking proper, i.e., with the rupture of complex molecules into more simple ones, when saturated hydrocarbons and their mixtures (oil fractions) are thermocatalytically treated. The main processes among them are:

dehydrogenation, or the removal of hydrogen with the conversion of saturated hydrocarbons into unsaturated ones;

aromatization of alkanes and cycloalkanes with their conversion into aromatic hydrocarbons;

isomerization, or the rearrangement of the carbon skeleton, e.g., the conversion of pentane into isopentane:



Alkane molecules disintegrate into elements under the action of even higher temperatures (1000°C and higher).

2.7. Methane. Natural Gas. The simplest paraffin hydrocarbon, *methane* CH_4, has various names which indicate where it is found in nature. The name *marsh gas* is connected with the formation of methane by the decay of vegetable matter on the bottom of marshes. It occurs in coal mines, and hence its name *mine gas* or *firedamp*. It can cause dangerous explosives when it accumulates in mines.

The atmosphere of large planets (Saturn, Jupiter) contains much methane, indicating that methane can originate under natural conditions even when there is no organic life.

One of the theories of the origin of life says that life began when the Earth was surrounded by an atmosphere of CH_4, NH_3, H_2O and H_2. Solar energy and electric discharges promoted the disintegration of these molecules down to free radicals, which converted into complex organic compounds, including amino acids.

Large reserves of fuel gases are found in the interior of the Earth. They are in a free state, existing as *natural gas* (accumulations in the Earth's crust), or are dissolved in oil and underground waters, existing as *accompanying oil gases*. Natural gas contains up to 98 per cent of methane, plus ethane, propane and other gases as impurities. Accompanying oil gas is less rich in methane (30-80 per cent), but contains a considerably large amount of its homologues: ethane, 4-20 per cent; propane, 5-22 per cent; butanes 5-20 per cent, and also pentanes and other gases. Higher alkanes are in the petroleum composition.

Hundreds of new gas deposits have been discovered recently in the Soviet Union. The richest gas deposits are in West Siberia.

Extracted gas is used as fuel in the household and industry, and also as chemical raw material.

The average calorific value of one cubic metre of natural gas is more than 46,000 kJ; there is enough energy in one cubic metre of natural gas to smelt 30 kg of cast iron. The substitution of other types of fuel, particularly coal, for gas is very economical, because it is more expensive to mine coal than to extract gas, while the calorific value of coal is lower.

Natural gas is used as chemical raw material in the following industrial processes:

1. Preparing soot and hydrogen by methane pyrolysis:

$$CH_4 \xrightarrow{1000^\circ C} 2H_2 + C$$

Soot is employed as an additive to natural rubber in the production of rubber; it is used for preparing printer's ink, and so forth, while hydrogen, for carrying out various syntheses, such as ammonia synthesis.

2. The preparation of acetylene (for details, see Sec. 5.5):

$$2CH_4 \xrightarrow{1500^\circ C} C_2H_2 + 3H_2$$

3. The conversion of methane by water vapour into a mixture of carbon monoxide and hydrogen:

$$CH_4 + H_2O \xrightarrow{800^\circ C} CO + 3H_2$$

The mixture formed serves as raw material for obtaining gasoline, methyl alcohol, etc.

4. The oxidation of methane by air in the presence of catalysts gives methyl alcohol CH_3OH, formaldehyde HCHO, and formic acid HCOOH.

5. Obtaining hydrocyanic acid by pyrolysing a mixture of methane and ammonia in the presence of oxygen:

$$2CH_4 + 2NH_3 + 3O_2 \xrightarrow{1000°C} 2HCN + 6H_2O$$

6. The chlorination of methane makes it possible to obtain methyl chloride CH_3Cl, chloroform $CHCl_3$, and carbon tetrachloride CCl_4.

Chapter 3

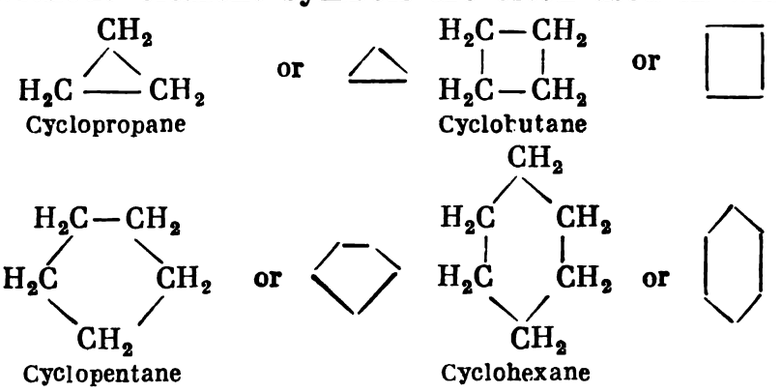
CYCLOALKANES

Compounds having closed chains are said to be cyclic (from the Greek "kyklos", meaning "circle").

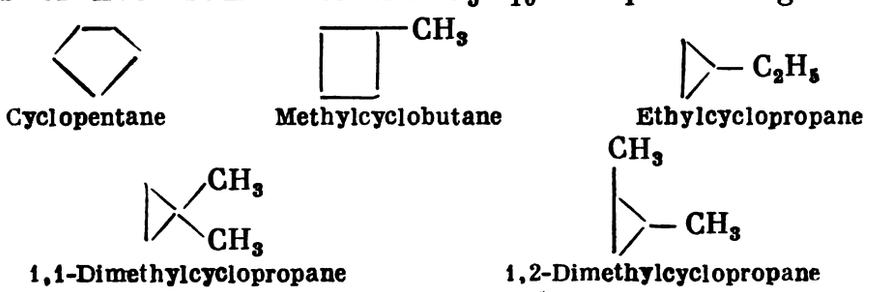
Molecules of unsubstituted *cycloalkanes* (*cycloparaffins*) consist of the CH_2 groups forming a ring; they are sometimes called *polymethylene hydrocarbons* from the name of the CH_2— group.

3.1. Structure of Cycloalkanes. Nomenclature. Isomerism. Occurrence in Nature. Structure, nomenclature. Carbon atoms are linked in cycloalkane molecules, like in alkane molecules, by σ-bonds (the state of sp^3 hybridization).

The general formula of the homologous series of cycloparaffins is $(CH_2)_n$ or C_nH_{2n}. Thus, the cycloparaffin molecule has two hydrogen atoms less than the paraffin molecule with the same number of carbon atoms. The name of cycloparaffins is formed by adding the prefix **cyclo** to the name of the corresponding paraffin. Conventional formulas without element symbols are often used in writing, e.g.,



Isomerism. The structural isomerism of cycloparaffins can be engendered by the size of the ring and by the dimensions and structure of side chains and their position. This is illustrated by the formulas of five isomers of the C_5H_{10} composition given below:



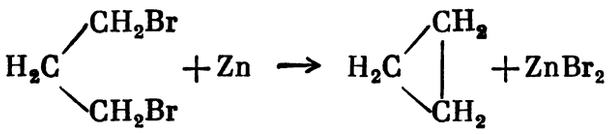
Cycloparaffins exhibit also stereoisomerism (see Sec. 3.5).

Cycloparaffins were studied by many Russian scientists. The most famous scientists in this field are V. V. Markovnikov, G. G. Gustavson, N. M. Kishner, N. D. Zelinsky, S. S. Nametkin, B. A. Kazansky and A. F. Plate.

Occurrence in nature. Cycloalkanes are found widely in nature: they are the main constituent of some oils (oil from Baku). Cycloparaffins were first detected in oil by V. V. Markovnikov, who called them *naphthenes*. It was later ascertained that compounds having five- and six-membered rings, i.e., cyclopentane and cyclohexane and their derivatives, are especially widespread in nature.

Cycloparaffins are found also in the essential oils of plants. The carbon skeleton of the cyclohexane homologue, l-methyl-4-isopropylcyclohexane, constitutes the basis of many *terpenes*, important natural compounds which will be considered separately.

3.2. Preparation of Cycloparaffins. A general method of preparing cycloparaffins is the action of metals on dihalogen derivatives of paraffins. For example, cyclopropane can be obtained from 1,3-dibromopropane under the action of zinc (Gustavson's synthesis):



Cyclobutane can thus be obtained from 1,4-dibromobutane. Metallic sodium is also used for these reactions.

The reactions of closing the ring often engender not the appropriate cycloparaffins, but their derivatives.

Compounds of the cyclohexane series are obtained in most cases by hydrogenating easily available compounds of the benzene series. An important example of such a reaction is the industrial production of pure cyclohexane from benzene:

$$C_6H_6 \xrightarrow[150\text{-}250^\circ C;\ 25\ kg/cm^2]{H_2/Ni;} C_6H_{12}$$

3.3. Ring Stability. A detailed study of cycloparaffins has shown that their chemical properties depend above all on the ring size. In this case, a distinction is usually made between compounds having small rings (C_3-C_4), common rings (C_5-C_7), medium rings (C_8-C_{11}), and large rings (from C_{12} onwards), which are called also *macrocyclic* compounds. A specific feature of small rings is their low stability as compared with other cyclic compounds. A higher content of energy in small rings is reflected particularly in the heats of com-

bustion, which have the following values per CH_2 group for various rings (in kJ/mole):

Cyclopropane	695	Cyclohexane . . .	657
Cyclobutane	686	Macrocycles . . .	657-660
Cyclopentane	661		

The heat of combustion of acyclic hydrocarbons per CH_2 group is 660 kJ/moles.

The first attempt to associate the stability of rings with the specific features of their structure was made by A. Baeyer (1835-1917).

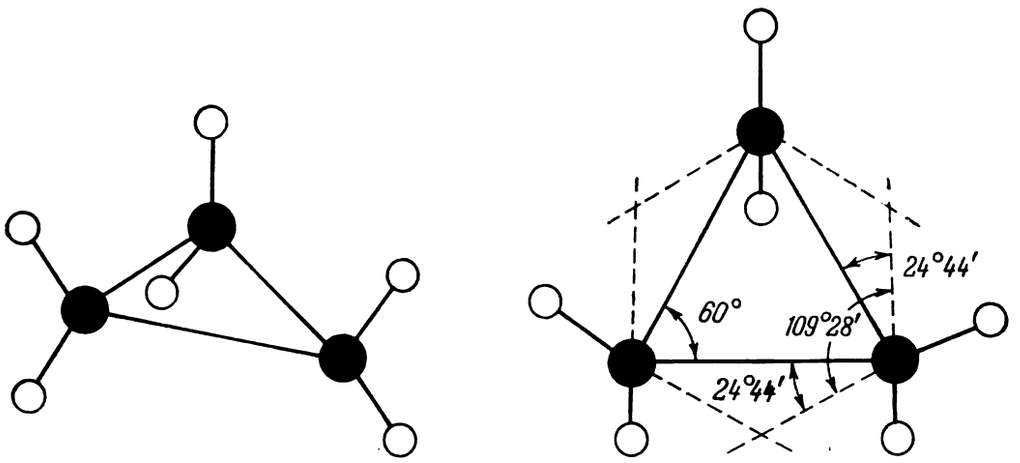


Fig. 3.1. Cyclopropane

He based his strain theory, put forward in 1885, on the tetrahedral model of the carbon atom, assuming that any distortion of valencies from their normal arrangement (at an angle of 109°28′) creates **strain** in the molecule and reduces its stability. According to Baeyer, a ring is a planar regular polygon. The simplest cyclic compound, cyclopropane, can be represented as an equilateral triangle with angles of 60° (Fig. 3.1). The distortion of valencies from their normal arrangement per bond (measure of strain α introduced by Baeyer) for the three-membered ring is:

$$\alpha = \frac{109°28' - 60°}{2} = 24°44'$$

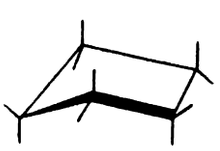
Baeyer believed that all rings have a planar structure, i.e., that all the carbon atoms lie on the same plane. We will see later that, in fact, this is not so. For planar rings of C_3-C_8, the calculated distortion of angles have the following values: cyclopropane, +24°44′; cyclobutane, +9°44′; cyclopentane, +0°44′; cyclohexane, −5°16′; cycloheptane, −9°33′, and cyclooctane, −12°46′. These figures correctly reflect a gradual increase in stability (i.e., a decrease in strain) from the three-membered ring to the five-membered

one. However, for rings with a greater number of members Baeyer's hypothesis no longer holds water: the six-membered ring is in fact stronger than the five-membered one, and an increase in strain is not observed also in macro cycles.

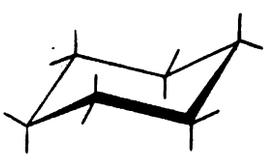
It has now been ascertained that only the three-membered ring is planar (three points are always on the same plane), and that angular strain is only one of the factors which must be taken into account when ring stability is being considered. Another important cause of strain is *eclipsing strain*, which is connected with the conformational state of a molecule.

Cyclopropane has an eclipsed conformation: six H—H interactions contribute to the higher inner energy of this cycle.

For cyclobutane and cyclopentane, there is the possibility of somewhat reducing the disadvantageous even numbers of H—H interaction by removing one of the carbons from the plane of the ring. For example, the most stable form for cyclopentane is the "envelope" I. The particularly high stability of cyclohexane is connected with the fact that it has neither angular strain nor eclipsing strain in the "chair" form II:



I



II

Rings having a still greater number of units are also nonplanar, and they have normal tetrahedral valence angles, however, when the units number 8-11 (medium rings), strain originates in them owing to the extremely close atomic packing, which causes a reaction not along the chemical bond chain, but directly through the ring.

3.4. Physical and Chemical Properties of Cycloalkanes. The physical properties of cycloparaffins are given in Table 3.1. The first two members of this series are gases, C_5-C_{10} are liquids, and the highest ones are solids. The boiling and melting points of cycloparaffins,

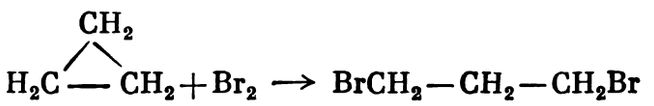
TABLE 3.1. **Physical Properties of Some Cycloparaffins**

Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Cyclopropane	C_3H_6	—127.4	—33.3	0.689 (at 40°C)
Cyclobutane	C_4H_8	—90.2	+12.9	0.703
Cyclopentane	C_5H_{10}	—93.8	49.3	0.745
Cyclohexane	C_6H_{12}	+6.5	80.7	0.779
Cyclononane	C_9H_{18}	11	178	0.850
Cyclotriacontane	$C_{30}H_{60}$	56	—	0.854

like their density, are somewhat higher than those of paraffins with an equal number of carbon atoms. Cycloparaffins, like paraffins, are practically water-insoluble.

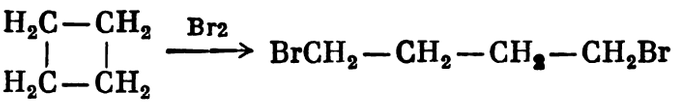
Chemically, small rings tend to undergo addition reactions, as a result of which the ring is ruptured and paraffins and their derivatives are formed; they are similar to unsaturated compounds in this respect. Rings with a larger number of units have a greater tendency to undergo substitution reactions, thus being similar to paraffins.

Reactions with halogens. Cyclopropane and its derivatives readily add bromine, opening the ring cycle and forming 1,3-dibromoderivatives of paraffins:

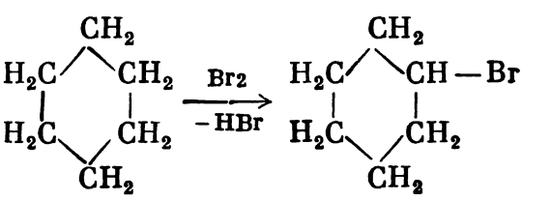


The reaction occurs more slowly than when propylene is used.

The higher stability of cyclobutane in comparison with cyclopropane is expressed in that it adds bromine even more slowly, i.e., only at elevated temperature, giving 1,4-dibromobutane:

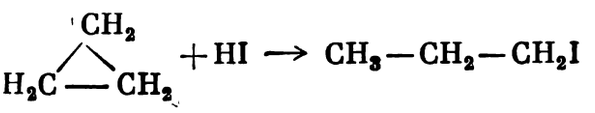


The rings of cyclopentane, cyclohexane and higher cycloalkanes are not opened under the action of halogens, but they undergo the substitution of hydrogen atoms for halogen:



Cyclohexane Bromocyclohexane

Reactions with hydrogen halides. Cyclopropane and its alkyl derivatives readily add hydrogen iodide, breaking the ring and forming alkyl iodide:

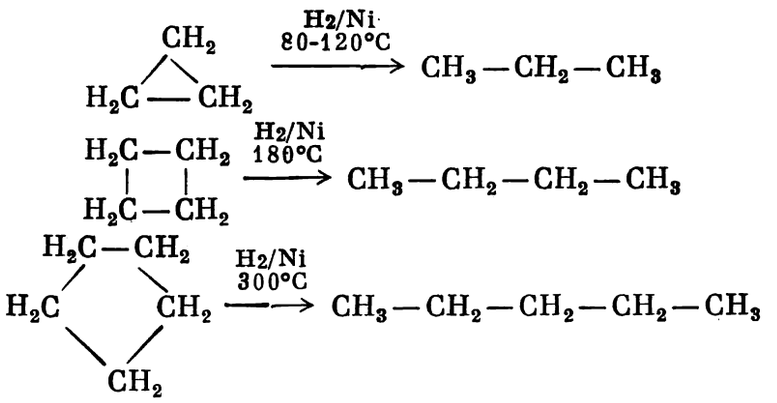


1-Iodopropane

When cyclobutane is used, this reaction occurs with greater difficulty on heating. Cyclopentane and the higher rings do not add hydrohalides.

Reaction with hydrogen illustrates well the gradual growth in the stability of rings from the three-membered to the six-membered one; an increasingly high temperature is required to break the rings under

the action of hydrogen over the nickel catalyst

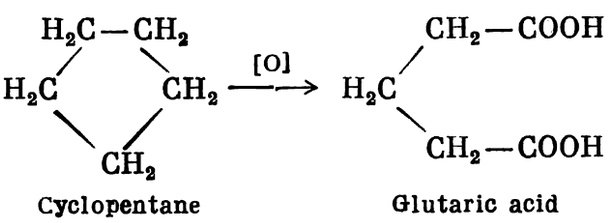


The cyclohexane ring is not broken under these conditions. Instead, *dehydrogenation* (hydrogen elimination) occurs with the formation of benzene:

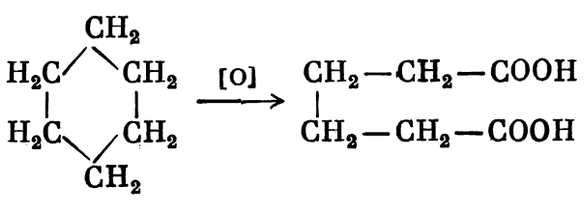
$$C_6H_{12} \longrightarrow C_6H_6 + 3H_2$$

Cyclohexane — Benzene

Oxidation. Cyclopropane and its derivatives are oxidized slowly at room temperature by a potassium permanganate solution in a neutral or an alkaline medium. Other cycloparaffins are also oxidized under the action of stronger oxidizing agents or on heating. In this case, the ring is opened and dibasic acids with the same number of carbon atoms in the molecule are formed:



Cyclopentane — Glutaric acid



Cyclohexane — Adipic acid

Nitration. Cycloparaffins having five- and six-membered rings are nitrated under the same conditions as paraffins. Nitrocyclohexane is practically important, because caprolactam may be obtained from it. Caprolactam is a raw material for producing the synthetic fibre capron (nylon 6).

According to modern concepts, the peculiar chemical behaviour of cyclopropane and cyclobutane in the homologous series of cycloalkanes is due to the special nature of bonds in the molecules of these compounds. In the cyclopropane molecule, the carbon-carbon and

carbon-hydrogen bonds differ from the ordinary σ-bonds of acyclic compounds. For example, the length of the carbon-carbon bond is equal to 0.1526 nm (while it is 0.154 nm in paraffins), and the valence angle does not deviate to the angles of an equilateral triangle, i.e., to 60°. The greatest electron density of the bond is not on the line which links the atomic centres, but on the outside of the triangle (curved, or "banana," form, Fig. 3.2).

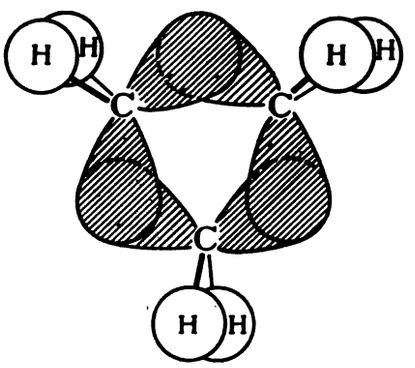
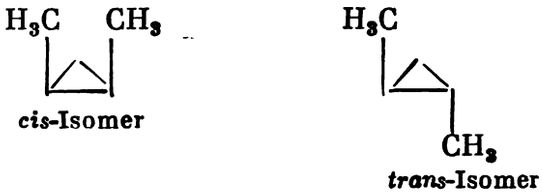


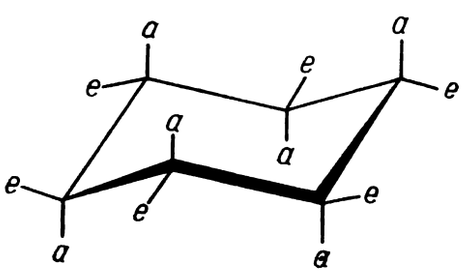
Fig. 3.2. "Banana bonds" of cyclopropane

3.5. Stereoisomerism of Substituted Rings. Spatial isomerism or stereoisomerism is exhibited in the existence of substances which have the same structural formula, but differ by the arrangement of atoms in space. The conformational state observed for ethane and other paraffins is an example of stereoisomerism, but individual conformations (conformers) are readily interconverted. There are also stable stereoisomers. In particular, they are known to exist also in the cycloparaffin series, where the phenomenon is caused by the different spatial arrangement of the side chains relative tothe ring. Such stereoisomerism is known as *geometric* or *cis-trans-isomerism.* An example is 1,2-dimethylcyclopropane, whose methyl groups can be on the same side (*cis-*) or on opposite sides (*trans-*) of the ring:

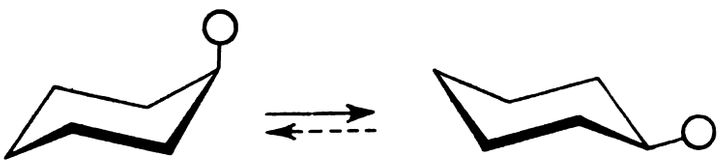


In cyclic compounds, there is no free rotation around the carbon-carbon bonds of the ring. *cis-trans*-Isomers cannot be readily interconvertible: for this purpose, the ring bonds must be broken. These isomers possess different physical and chemical properties.

Stereoisomerism in nonplanar rings is of even greater complexity. For example, the bonds of the carbon atoms of cyclohexane are divided into two types: *axial* ones (*a*), which are perpendicular to the ring, and *equatorial* ones (*e*), which are directed along the ring periphery:



The equatorial position of the substituent is more advantageous than the axial one, and therefore all the monosubstituted cyclohexanes have substituents in the equatorial position. The axial form, which can be represented as a ring originating due to a change in conformation (so-called *inversion*), has a greater reserve of energy, and therefore its existence is less probable:



Unstable conformation Stable conformation

3.6. Important Individual Cycloalkanes. *Cyclopentane* is contained in petroleum. It is used as a motor-fuel additive for enhancing the quality of the fuel, and is also employed in various syntheses.

Petroleum contains also the carboxyl derivatives of cyclopentane: *cyclopentanecarboxylic acid* and *its homologues*, which are known as *naphthenic acids*. When petroleum products are being purified with alkali, sodium salts of these acids that possess detergency (*naphthene soap*) are formed.

Cyclohexane is contained in petroleum, and it can also be prepared by hydrogenating benzene over nickel or platinum catalysts. The purity of cyclohexane obtained by this technique is 99.99 per cent and even higher. Cyclohexane is used mainly for synthesizing adipic acid (see Sec. 12.12) and caprolactam, which are intermediate products for manufacturing the synthetic fibres of nylon 66 and nylon 6 (capron) (see Sec. 23.7). The most important derivatives of cyclohexane are the alcohol called *cyclohexanol* and the ketone known as *cyclohexanone*.

Chapter 4

ALKENES

Alkenes are unsaturated hydrocarbons containing one double bond in the molecule. The simplest member of such hydrocarbons is *ethylene*, C_2H_4, and hence the compounds of this series are also called hydrocarbons of the ethylene series. The name *olefins* is often used for them.

The name "olefins" is derived from the Latin name of ethylene, "gaz olefiant", which means "oil-making" gas. This name was given to ethylene in the eighteenth century by Dutch chemists owing to its ability to form with chlorine a liquid oily substance known as ethylene chloride, $C_2H_4Cl_2$.

Homologues of ethylene are propylene C_3H_6, butylene C_4H_8, pentene C_5H_{10}, hexene C_6H_{12}, and others.

The homologous series of ethylene hydrocarbons has the general formula of C_nH_{2n}, i.e., the same as that of the cycloparaffin series. Thus, olefins and cycloparaffins are isomers relating to different homologous series.

4.1. Structure of Alkenes. A characteristic feature of the alkene structure is the presence of *one double* carbon-carbon bond $>C=C<$ in the molecule.

The double bond is formed by *two pairs* of shared electrons (*tetraelectron bond*). Carbon atoms linked by a double bond are in a state of sp^2 hybridization, and each of them forms *three* σ-*bonds* which lie on the same plane at an angle of 120°. Unhybridized orbitals of *p*-electrons are perpendicular to the plane of the σ-bond and are parallel to one another, and they form a second bond, known as the π-bond (the electrons are called π-electrons), as a result of "side" overlap. The electron cloud of the π-bond is partially *above* and partially *below* the plane on which atoms lie. Thus, two pairs of electrons form σ- and π-bonds which are different by their nature, geometry and strength. The double bond is a combination of σ- and π-bonds (σ + π-bond). The side overlap of unhybridized *p*-orbitals forming the π-bond brings the carbon atoms closer together and the distance between them becomes shorter: the length of the double C=C bond is 0.133 nm (the length of the simple C—C bond is 0.154 nm). The arrangement of atoms and bonds in the ethylene molecule is illustrated in Fig. 4.1. The effect of the nature of the double bond

on alkene properties will be dealt with when their chemical properties will be considered (see Sec. 4.4).

The concept that the double bond consists of two different bonds (σ- and π-bonds) is only a hypothesis, although it conforms well with empirical data. There is no direct evidence of the correctness of such a model. Moreover, the distinguished American scientist L. Pauling proposed to use a different model for describing olefin

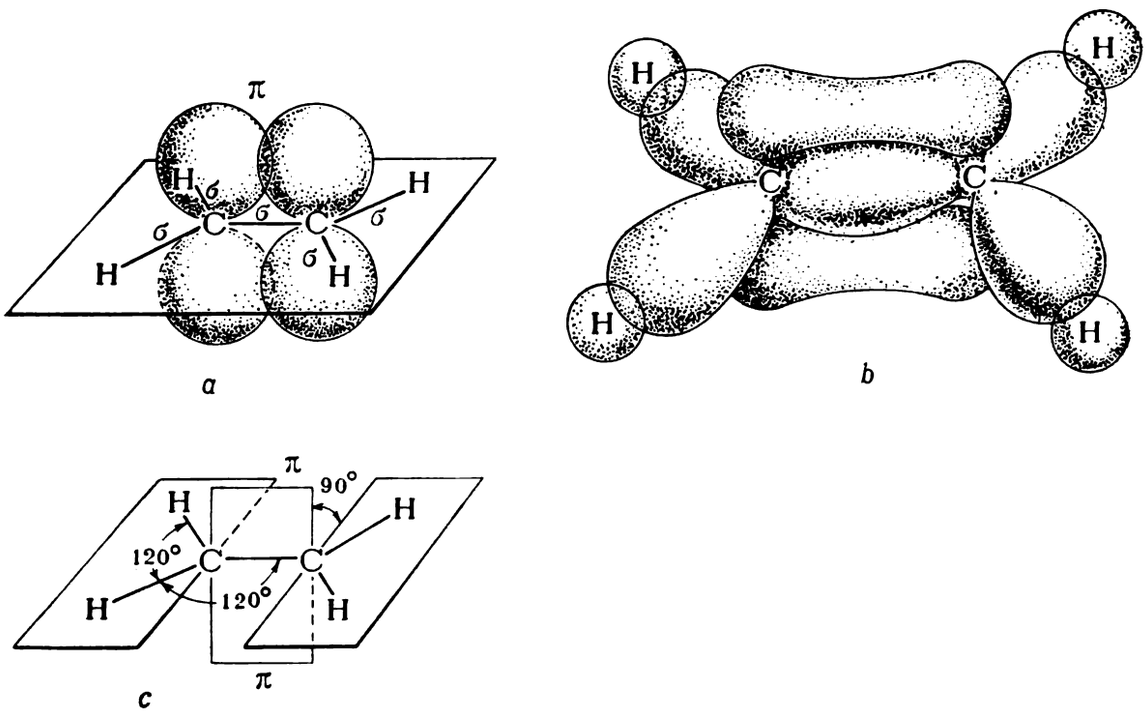


Fig. 4.1. Structure of ethylene in different representations:
a—σ-bonds and *p*-electron clouds; *b*—σ-bonds and the π-bond; *c*—geometry of the molecule

properties. In this model, it is taken that the double bond is formed by *two same bonds* (they are known as "τ-bonds", or "*banana bonds*" owing to their curved form). Basing his calculations on such a model, Pauling succeeded in describing the properties of the double bond just as well as is done by means of the σ-π-model.

4.2. Isomerism and Nomenclature of Alkenes. Structural isomerism. Structural isomers of alkenes can differ by the branchings of the carbon chain (isomerism of the carbon skeleton) and by the position of the double bond (position isomerism). The first of the ethylene hydrocarbons for which isomers are possible has four carbon atoms. The trivial name of this hydrocarbon is *butylene*, C_4H_8. Three isomers are known for it:

Isomerism of the carbon skeleton:

- $CH_2=CH-CH_2-CH_3$ } Position isomerism of the double bond
- $CH_3-CH=CH-CH_3$ }
- $CH_2=C(CH_3)-CH_3$

The hydrocarbon pentene, C_5H_{10}, has five isomers:

Isomerism of the carbon skeleton

$CH_2=CH-CH_2-CH_2-CH_3$

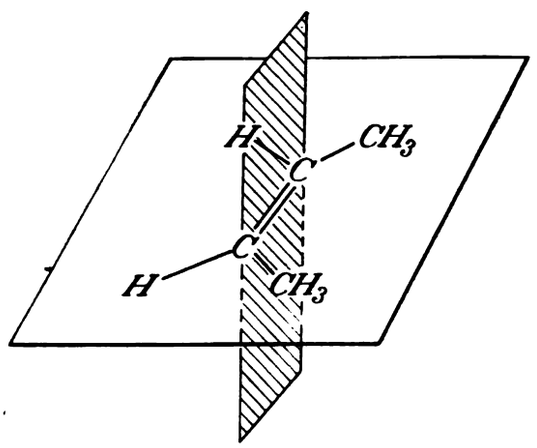
$CH_3-CH=CH-CH_2-CH_3$

$CH_2=C(CH_3)-CH_2-CH_3$ $\quad$ $CH_3-C(CH_3)=CH-CH_3$

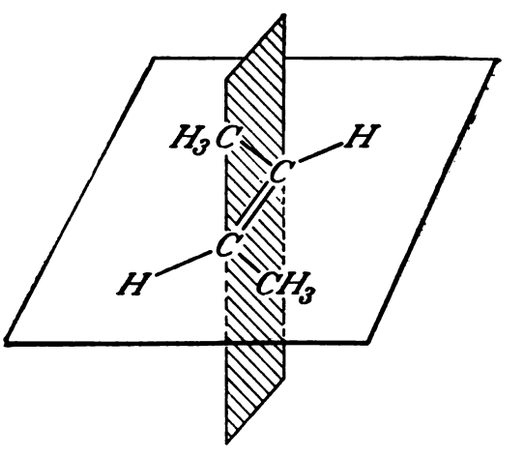
$CH_3-CH(CH_3)-CH=CH_2$

Position isomerism of the double bond

cis-trans-**Isomerism.** For ethylenic compounds, another type of isomerism is possible; it is known as *stereoisomerism*, which depends on the arrangement of the substituents relative to the double bond. This isomerism is observed when each of the carbon atoms linked by the double bond spends the remaining two valencies on the bond with two *different* substituents. The arrangement of these substituents on the same side of the double bond gives the *cis-isomer*, and on opposite sides, the *trans-isomer*, e.g.,



cis-Isomer
(m.p −139.3°C)
(b.p.+3.70°C)



trans-Isomer
(m.p.−105.8°C)
(b.p.+0.96°C)

The interconversion of these isomers requires rotation around th double carbon-carbon bond, i.e., it is necessary to disturb the overlap of the *p*-orbitals and rupture the π-bond. It is necessary to spend more than 250 kJ/mole of energy. Such an energy barrier hinders rotation and causes the existence of *cis-trans*-isomers.

As a rule, *trans*-isomers are more stable and have a higher melting point. On heating, *cis-trans*-isomers can turn into one another: equilibrium is established between them. The characteristic features of this type of stereoisomerism will be considered in greater detail by

taking the example of unsaturated carboxylic acids: fumaric and maleic acids (see Sec. 12.12).

Nomenclature. The trivial names of olefins are characterized by the ending **ylene**: ethylene, propylene, butylene, etc.

Rational nomenclature regards ethylenic hydrocarbons as ethylene derivatives, which contain hydrocarbon radicals instead of hydrogen atoms. If need be, the position of radicals at different atoms of the ethylene grouping is specified, denoting them by the Greek letters α and β, e.g.,

I. $CH_2=CH-CH_2-CH_3$ . . . . . Ethylethylene

II. $CH_3-CH=CH-CH_3$ . . . . . *sym*-Dimethylethylene or α,β-Dimethylethylene

III. $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$ . . . . . *unsym*-Dimethylethylene or α,α-Dimethylethylene

IV. $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH=CH_2$ . . . . Isobutylethylene

According to modern international rules, the names of alkenes are constructed similarly to those of alkanes, but the ending **ane** is replaced by the ending **ene** (hence the general name *alkenes*).

The position of the double bond is indicated by a figure that corresponds to the carbon atom from which the double bond begins. A chain which includes the double bond is selected as the principal chain even if it is not the longest. The numbering is done in a way that the carbon atom from which the double bond begins has the smallest number.

The foregoing structures I—IV have the following names by such nomenclature: I—1-butene, II—2-butene, III—2-methyl-1-propene, IV—4-methyl-1-pentene. The application of such nomenclature can be exemplified by several other compounds:

$CH_3-CH=CH-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$

4-Methyl-2-pentene

$CH_3-CH_2-CH_2-\overset{\displaystyle CH_2}{\overset{\|}{C}}-CH_2-CH_3$

2-Ethyl-1-pentene

The general name of the radicals formed from alkenes is *alkenyls*. The names of several radicals seen most frequently are given as an example:

$CH_2=CH-$ . . . . . Vinyl (Ethenyl)

$CH_2=CH-CH_2-$ . . . Allyl

$CH_3-CH=CH-$ . . Propenyl

$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-$ . . Isopropenyl

4.3. Preparation of Alkenes. Olefins, unlike paraffins, are rarely found in nature. Lower olefins in small amounts can be in the composition of oil gas, and higher ones occur as minor constituents of petroleum (Canadian oil). The most important industrial supplier of olefins is the petroleum refining. Large amounts of olefins are formed in *cracking* and *pyrolysis of petroleum*. The gases which are obtained up to 25 per cent from petroleum cracking are rich in lower gaseous olefins C_2-C_4. Cracked benzines contain many liquid olefins.

Higher alkanes undergo cleavage under the action of high temperatures (400-700°C). As we have already seen (Sec. 2.5), the homolytic cleavage reaction occurs with the formation of free radicals:

$$CH_3—CH_3 \longrightarrow 2CH_3\bullet \quad RCH_2—CH_2R \longrightarrow 2RCH_2\bullet$$

The radical ($CH_3\cdot$, $RCH_2\cdot$), formed as a result of the primary rupture of the C—C bond, attacks the molecule of higher paraffin and abstracts hydrogen from the tertiary or secondary carbon atom, which is removed from the chain end:

$$CH_3\bullet + CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3 \longrightarrow$$
$$\longrightarrow CH_4 + CH_3—CH_2—\dot{C}H—CH_2—CH_2—CH_2—CH_2—CH_2—CH$$

Then comes the breakdown of the molecule in the β-position towards the carbon atom, which carries an unpaired electron; in this case, olefin and a new radical are formed:

$$CH_3—CH_2—\dot{C}H—CH_2—|CH_2—CH_2—CH_2—CH_2—CH_3 \longrightarrow$$
$$\longrightarrow CH_3—CH_2—CH=CH_2 + \bullet CH_2—CH_2—CH_2—CH_2—CH_3$$

Multiple β-cleavage engenders a large amount of olefins, particularly ethylene:

$$\bullet CH_2—CH_2—|CH_2—CH_2—CH_3 \longrightarrow CH_2=CH_2 + \bullet CH_2—CH_2—CH_3$$
$$\bullet CH_2—CH_2—|CH_3 \longrightarrow CH_2=CH_2 + CH_3\bullet$$

Lower saturated hydrocarbons and hydrogen are formed simultaneously. For example, the following hydrocarbons are formed from butane, C_4H_{10}, at 600°C and standard pressure:

$$CH_3—CH_2—CH_2—CH_3 \begin{cases} \longrightarrow CH_4 + CH_2=CH—CH_3 & (48\%) \\ \longrightarrow CH_3—CH_3 + CH_2=CH_2 & (36\%) \\ \longrightarrow H_2 + CH_3—CH=CH—CH_3 & (16\%) \end{cases}$$

Table 4.1 gives the composition of the gaseous products of petroleum refining.

Another important industrial method of preparing olefins is *paraffin dehydrogenation*. The catalyst in this case is chromium oxide.

TABLE 4.1. **Composition of Gaseous Products Formed by Different Methods of Petroleum Refining**

Components	Content, %			
	direct distillation	pyrolysis	thermal cracking	catalytic cracking
Hydrogen	1	12	3-9	5-6
Methane	11-46	55-57	28-50	10
Ethane	3-17	5-7	13-18	3-5
Propane	3-28	0.5	3-15	18-20
Butane	14-34	0.2	1-6	42-46
Ethylene	—	16-18	2-23	3
Propylene	—	7-8	6-18	6-11
Butylene	—	4-5	4-10	5-6

The process is carried out at 450-460°C:

$$CH_3-CH_2-CH_2-CH_3 \begin{cases} \rightarrow CH_2=CH-CH_2-CH_3+H_2 \\ \rightarrow CH_3-CH=CH-CH_3+H_2 \end{cases}$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2+H_2$$

1-Alkenes having an even number of carbon atoms are obtained from ethylene (ionic polymerization) and used for producing synthetic *detergents.*

The *laboratory methods* of preparing olefins are largely elimination reactions. The most important one is *dehydration of alcohols* (water removal). Water is eliminated at elevated temperature when alcohols with dehydrating substances (concentrated sulphuric or phosphoric acid) are heated, or alcohol vapours are passed over such catalysts as kaolin, aluminium and thorium oxides. For example, ethylene is obtained from ethyl alcohol:

$$CH_3-CH_2OH \xrightarrow[-H_2O]{} CH_2=CH_2$$

In alcohol dehydration, hydrogen is eliminated mainly by *Zaitsev's rule* (1875), i.e., from one of the adjacent carbon atoms that is the poorest in hydrogen:

$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{} CH_3-CH=CH-CH_3$$

Dehydrohalogenation. Hydrogen halide is eliminated (also by Zaitsev's rule) on heating alkyl halides with concentrated alcoholic solutions of alkalies or organic bases. The reaction occurs most

readily with tertiary halogen derivatives, and with greater difficulty with primary ones:

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHI-CH_3 \xrightarrow[-HI]{\text{KOH (alcoholic solution)}} \rightarrow CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$$

Olefins can also be obtained by eliminating halogen from dihalogen derivatives, where halogens are attached to the adjacent carbon atoms (*dehalogenation*):

$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[-ZnBr_2]{\text{zinc dust}} CH_3-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

4.4. General Characteristics of Physical and Chemical Properties. Physical properties. Olefins are similar to the corresponding paraffins by their physical properties, but their boiling points are somewhat lower, while their density, somewhat higher. The first three members of the series C_2-C_4 are gases; from C_5 to C_{17}, the members are liquids, and from C_{18} onwards, they are solids. The isomerism of the carbon chain, that of the double bond position and the spatial configuration are reflected in the physical constants of isomers (Table 4.2).

TABLE 4.2. **Physical Properties of Some Alkenes**

Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20} (at b.p.)
Ethylene	$CH_2=CH_2$	−169	−105	0.570
Propylene	$CH_2=CH-CH_3$	−185.2	−47.8	0.610
α-Butylene (1-butene)	$CH_2=CH-CH_2-CH_3$	−130.0	−6.3	0.595
β-Butylene (2-butene)	$CH_3-CH=CH-CH_3$			
cis-		−138.9	+3.5	0.621
trans-		−105.5	+0.9	0.604*
Isobutylene	$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$	−140	−6.9	0.594

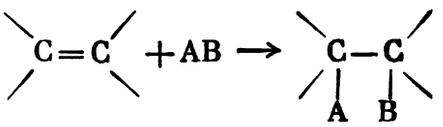
* Under pressure.

All the olefins have a density which is less than unity and possess a peculiar odour; they dissolve poorly in water, but much better than the corresponding paraffins.

Chemical properties. The chemical behaviour of alkenes is determined by the presence of the double bond, especially by the spatial direction of the σ- and π-bonds.

The electron density of the σ-bond is concentrated along the line which connects the atomic nuclei, while that of the π-bond is beyond these limits, forming a larger region of the negative charge. A characteristic feature of π-electrons is their mobility; they are held less firmly than the σ-electrons by the atomic nuclei. Therefore, the π-bond is polarized more readily. The electrons which form the π-bond are readily drawn into chemical reactions by electrophiles, which, while exciting the polarization of the π-bond, cause its heterolytic cleavage. The difference in the energies of the (σ + π)-bond and of the σ-bond is about 270 kJ/mole and characterizes the measure of strength of the π-bond. When the π-bond is ruptured, addition reactions occur with the formation of *two new* σ-bonds. Addition reactions are typical of olefins.

4.5. Alkene Reactions. Addition reactions. A general scheme of reactions of addition along the double bond is given below:

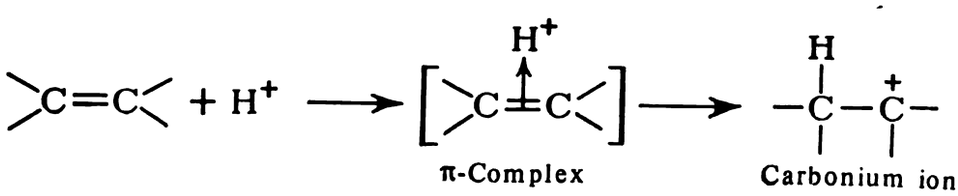


Thus, the process formally consists in the rupture of the double bond and the addition of the "fragments" of a reagent to the freed valencies of two adjacent carbon atoms. Hydrogen, halogens, hydrogen halides, sulphuric acid, hydroxyl groups (in oxidation reactions), oxygen and various organic substances can be added to the double carbon-carbon bonds by this scheme.

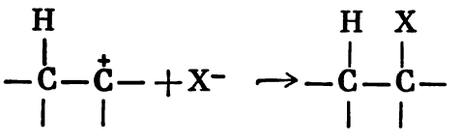
The larger part of addition reactions to the double carbon-carbon bond is of a heterolytic type and relates to *electrophilic addition* reactions.

The process of electrophilic addition is a *stepwise ionic process.* The determining stage of such reactions is the interaction between the electrophilic reagent and the π-electron cloud of the double bond. The electrophilic reagent is in most cases the proton H^+, which is formed when mineral acids (HCl, HBr, HI, H_2SO_4) are dissociated. At first, the electrophilic reagent, owing to its positive charge, reacts with the π-electrons of the double bond, forming the *π-complex.* Then, an ordinary σ-bond is formed with one of the unsaturated carbon atoms at the expense of the π-electrons of the double bond. The adjacent carbon atom, the second partner of the existing double

bond, becomes positively charged after losing an electron:



At the second, concluding stage, the carbonium ion reacts with the anion X^-, forming the second σ-bond. As a result, the end product of addition is obtained:



The first stage usually occurs more slowly than the second one.

Let us consider a typical example of such reactions, i.e., the addition of hydrogen bromide to 2-butene:

$$HBr \rightleftharpoons H^+ + Br^-$$

$$CH_3-CH=CH-CH_3 + H^+ \longrightarrow [CH_3-CH^{+}\!\!-CH-CH_3] \longrightarrow$$

$$\longrightarrow CH_3-CH_2-\overset{+}{C}H-CH_3$$

$$CH_3-CH_2-\overset{+}{C}H-CH_3 + Br^- \longrightarrow CH_3-CH_2-CHBr-CH_3$$

Thus, the addition of hydrogen bromide is a two-stage ionic process. The determining stage of the entire reaction is the addition of a proton with the formation of the carbonium ion. This is proven by the fact that hydrogen halides, and not their salts, are capable of being added.

Halogens are added also by the electrophilic mechanism. In this case, the distribution of the electron density in the halogen molecule changes in the first place, i.e., the molecule is polarized, under the action of the electron density of the double bond. The electrophilic nature of a symmetrical halogen molecule can be exhibited only after polarization. The reaction then occurs in the way described above:

$$CH_2=CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \longrightarrow \overset{+}{C}H_2-CH_2Br \xrightarrow{Br^-} BrCH_2-CH_2Br$$

Other inorganic substances (H_2SO_4, H_2O, HOCl, etc.) and some organic molecules are also added similarly. After the initial addition of the electrophilic particle, any anion which is in a solution

can be added at the second stage. This was proven by the reaction between ethylene and bromine in an aqueous solution in the presence of the anions Cl^- and NO_3^-. In this case, besides $BrCH_2—CH_2Br$, the following compounds are obtained: $BrCH_2—CH_2Cl$, $BrCH_2—CH_2ONO_2$.

The structure of the olefin molecule, and also the reagent nature, affect the reaction rate. Let us consider some specific examples of the alkene addition reactions.

1. Halogen addition. Olefins add halogens and, especially readily, chlorine and bromine under ordinary conditions. As a result, dihalogen derivatives of paraffins are formed; they contain halogens bonded to adjacent carbon atoms, and are known as *vicinal* derivatives (from the Latin "vicinalis", meaning "neighbouring"):

$$CH_2=CH_2+Cl_2 \longrightarrow \underset{\text{1,2-Dichloroethane}}{ClCH_2—CH_2Cl}$$

$$CH_3—CH=CH_2+Br_2 \longrightarrow \underset{\text{1,2-Dibromopropane}}{CH_3—CHBr—CH_2Br}$$

Thus, the decolorization of bromine water is a qualitative reaction for the double bond. The halogen addition reaction is used also for quantitatively determining the degree of unsaturation. For this, use is made of the solution of bromine in carbon tetrachloride or chloroform, and the solutions of iodine chloride or bromine chloride. The latter are added along the double bond especially readily, because the molecule itself is already polarized owing to the difference in the electronegativity of both atoms:

$$\overset{\delta-}{Cl}—\overset{\delta+}{I} \qquad \overset{\delta-}{Cl}—\overset{\delta+}{Br}$$

Methods based on the addition of halogens along the double bond are important for determining the degree of unsaturation of liquid fats and oils. The reaction between ethylene and chlorine is used industrially for obtaining dichloroethane, which is employed as a solvent; the reaction is also used for producing vinyl chloride.

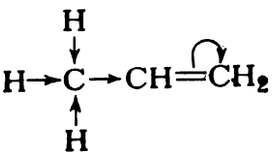
2. Addition of hydrogen halides (hydrohalogenation). The addition reactions of unsymmetrical reagents of the HX type to unsymmetrical olefins, e.g., $RCH=CH_2$, beg the question of the order of addition. In the general scheme under consideration, the matter in question is consequently whether the compound $RCHX—CH_3$ or the compound $RCH_2—CH_2X$ is formed.

The regularities of such reactions were studied by V. V. Markovnikov (1838-1904), who took the example of the addition of hydrohalides to olefins. As a result of this work, *Markovnikov's rule* (1869) was formulated: when hydrogen halides are added to unsymmetrical olefins, hydrogen becomes attached to the carbon atom which carries the largest number of hydrogen atoms, while halogen attaches

itself to the other carbon atom linked to the first one by a double bond, i.e., the atom which has the smallest number of H atoms:

$$CH_3-CH=CH_2+HBr \longrightarrow CH_3-CHBr-CH_3$$

Markovnikov's rule is now explained by the electron theory of organic reactions. Carbon in the methyl group CH_3 carries a certain negative charge, because the electronegativity of carbon is greater than that of hydrogen. This causes the σ-electrons of the H_3C-CH bond to shift towards the central carbon atom. In turn, the shift causes a far greater displacement of mobile π-electrons of the double bond in the direction indicated by the curved arrow:



Thus, the electron shifts $H\rightarrow C$ and $H_3C\rightarrow CH$ cause a great shift in the electrons of the double bond, i.e., they cause polarization with a shift in electron density towards the carbon atom which is not linked with the alkyl group:

$$CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2$$

The proton is added to the carbon atom which carries a partial negative charge. It follows that this atom will be the one which is linked with a smaller number of alkyl groups (the one which is more saturated with hydrogen). The anionic part of the reagent is directed towards the carbon atom which has the least electron density, i.e., towards the least hydrogenated carbon atom.

The stability of the carbonium ion formed intermediately also affects the result of the reaction. It should be taken into account that two carbonium ions could be formed at the first stage of the reaction, depending on the unsaturated carbon atom to which the proton is directed:

$$\underset{\text{I}}{CH_3-CH_2-\overset{+}{C}H_2} \quad \text{or} \quad \underset{\text{II}}{CH_3-\overset{+}{C}H-CH_3}$$

The direction which requires less energy is preferable. In carbonium ion II, the positive charge on the central atom is partially extinguished by two methyl groups on whose carbon atoms is δ^-. As a result, the positive charge is "spread out" on three carbon atoms. The charge of the centre of the carbonium ion in structure I will be higher than that in structure II, because the carbon atom which bears the charge is linked only with one radical (ethyl). The cation of greater stability is the one which has less energy, or carbonium ion II; in this case, hydrogen is added to the carbon atom which is more hydrogenated.

Markovnikov's rule is observed only for the *ionic mechanism* of addition. It can be formulated in the following way: the electropositive (cationic) particle of the reagent is added to the carbon atom which contains a larger number of hydrogen atoms, while the electronegative (anionic) particle, to the more substituted carbon atom, e.g.,

$$CH_3-CH=CH_2+\overset{\delta+}{I}-\overset{\delta-}{Cl} \longrightarrow CH_3-CHCl-CH_2I$$

Iodine chloride

Several electrophilic reagents and their cationic and anionic parts are given below:

Cation	H	H	H	H	H	Cl	$HgOCOCH_3$	I
Anion	Cl	Br	I	$HOSO_2O$	HO	HO	CH_3COO	Cl

Markovnikov's rule is not ideal. Although the order of addition is determined above all by the structure of the olefin molecule, it also depends on the reaction conditions. For instance, in the presence of peroxides, the reaction becomes radical, and addition contradicts Markovnikov's rule. Further exposition will show that the rule is inapplicable to some unsaturated aldehydes and acids.

3. Addition of sulphuric acid. This reaction occurs similarly to addition of hydrogen halides. As a result, alkyl sulphuric acids (acid esters of sulphuric acid) are formed:

$$CH_2=CH_2+HOSO_2OH \longrightarrow \underset{\text{Ethylsulphuric acid}}{CH_3-CH_2-O-SO_2OH}$$

4. Water addition (olefin hydration). The direct addition of water to olefins (direct hydration) is carried out in the presence of phosphate catalysts (H_3PO_4 on aluminosilicate with salts of cadmium, copper and cobalt; 300°C; 80 kg/cm^2):

$$CH_2=CH_2+H_2O \longrightarrow CH_3-CH_2OH$$

Alcohols can be obtained also by hydrolyzing alkyl sulphuric acids (sulphuric acid hydration):

$$CH_3-CH_2-OSO_2OH+H_2O \longrightarrow CH_3-CH_2OH+HOSO_2OH$$

5. Hydrogenation. Olefins do not add nascent hydrogen, and therefore such reagents as zinc and acid, sodium and alcohol do not act on them. However, by hydrogen treatment in the presence of

catalysts, olefins can be *catalytically hydrogenated* into paraffins:

$$CH_2=CH_2 \xrightarrow{H_2/Pt} CH_3-CH_3$$

Ethylene — Ethane

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \xrightarrow{H_2/Ni} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_3$$

2,4,4-Trimethyl-2-pentene — 2,2,4-Trimethylpentane

The most active catalysts of this reaction are platinum and palladium, but finely divided nickel is used more frequently in practice. "Raney nickel" is an especially active form of the nickel catalyst.

To prepare Raney nickel, the aluminium-nickel alloy is treated with alkali; in this case, aluminium passes into solution as aluminate, while nickel remains in the form of a black powder having a developed surface, which is important in the exhibition of catalytic properties.

Alkylation reactions. Organic substances, such as alcohols and carboxylic acids, can be added along the double bond with the aid of an appropriate catalyst.

A very important reaction in modern industrial organic synthesis is the alkylation of alkanes by olefins. This reaction consists in the addition of an alkane (mainly with a tertiary carbon atom) along the double bond of an olefin. The catalysts of reactions are sulphuric and hydrofluoric acids, boron trifluoride and aluminium chloride:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-H+CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_3$$

Isooctane

The mechanism of the reaction is:

$$CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH_2+H^+ \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^+}}}$$

$$(CH_3)_3C^+ + CH_2=C(CH_3)_2 \longrightarrow (CH_3)_3C-CH_2-\overset{+}{C}(CH_3)_2$$

$$(CH_3)_3C-CH_2-\overset{+}{C}(CH_3)_2 + CH(CH_3)_3 \longrightarrow (CH_3)_3C-CH_2-CH(CH_3)_2 + (CH_3)_3C^+$$

The branched paraffins thus obtained are valuable components for high-octane gasolines.

Polymerization reactions. Olefin molecules can be made to add each other. An example is the reaction of **dimerization** of isobutylene

under the action of concentrated sulphuric acid, discovered by Butlerov. In this reaction, the isobutylene molecule in the acid medium adds a proton at the expense of the electrons of the double bond. The carbonium ion formed is added as an electrophilic particle along the double bond by the second olefin molecule.The addition product becomes stabilized, ejecting the proton; in this case, the double bond can have two different positions in the unsaturated hydrocarbon with eight carbon atoms. This synthesis is now performed on an industrial scale. The mixture of isomeric hydrocarbons obtained is then subjected to catalytic hydrogenation in order to synthesize isooctane:

$$(CH_3)_2C=CH_2 \xrightarrow{H^+} (CH_3)_3C^+ \xrightarrow{CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3} (CH_3)_3C-CH_2-\overset{+}{C}(CH_3)_2 \xrightarrow[-H^+]{}$$

$$\rightarrow (CH_3)_3C-CH_2-\underset{CH_3}{\overset{|}{C}}=CH_2+(CH_3)_3C-CH=C(CH_3)_2 \xrightarrow{H_2}$$

$$\rightarrow (CH_3)_3C-CH_2-CH(CH_3)_2$$

Isooctane

Thus, the by-product of oil cracking, isobutylene gas, is converted into valuable liquid fuel for internal-combustion engines.

Addition products of a larger number of molecules, **polymers**, can also be obtained:

$$\ldots+CH_2=CH_2+CH_2=CH_2+\ldots \rightarrow \ldots-CH_2-CH_2-CH_2-CH_2-\ldots$$

or

$$x(CH_2=CH_2) \rightarrow (-CH_2-CH_2-)_x$$

The high-molecular-weight polymer of ethylene is called *polyethylene.*

Lower olefins, i.e., ethylene, propylene and isobutylene, are very important monomers. Their polymerization products are used for producing plastics, synthetic fibres and other practically important materials. This is considered in greater detail in Sec. 23.3.

Action of oxidizing agents. Alkenes are readily subjected to the action of various oxidizing agents, greatly differing in this respect from paraffins and cycloparaffins. Various products are formed, depending on the oxidation conditions. Olefins turn into carbon dioxide and water under the most severe conditions, when combustion is effected in the atmosphere:

$$C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$$

Under milder conditions, oxidation occurs above all across the double bond.

Diatomic alcohols, glycols, are formed when oxidation is carefully effected by the alkaline solution of potassium permanganate:

$$CH_2=CH_2 \xrightarrow{KMnO_4;\ (O+H_2O)} HO-CH_2-CH_2-OH$$

This reaction was discovered by the Russian chemist E. E. Wagner (1849-1904). The reaction occurs rapidly and in the cold, and permanganate loses its characteristic colour. Wagner's reaction is a qualitative test for the presence of the double bond.

The oxidative cleavage of the olefin molecule across the double bond occurs under the action of more energetic oxidizing agents (acid solution of permanganate, chromic acid mixture). The oxidation reactions of three isomeric butylenes are given as examples:

$$\underset{\text{1-Butene}}{CH_3-CH_2-CH=CH_2} \xrightarrow{[O]} \underset{\text{Propionic acid}}{CH_3-CH_2-COOH}+CO_2 \qquad (1)$$

$$\underset{\text{2-Butene}}{CH_3-CH=CH-CH_3} \xrightarrow{[O]} \underset{\text{Acetic acid}}{2CH_3-COOH} \qquad (2)$$

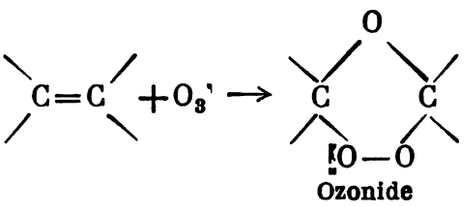
$$\underset{\text{2-Methylpropene (isobutylene)}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2} \xrightarrow{[O]} \underset{\text{Acetone}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=O}+CO_2 \qquad (3)$$

The position of the double bond in a molecule and the structure of the carbon skeleton can be determined by the oxidation products. For example, if carbon dioxide is formed in oxidation together with carboxylic acid, it can be concluded that the double bond was at the end (reactions 1 and 3). But if only carboxylic acids are formed, the olefin apparently had the structure of R—CH=CH—R (reaction 2), because it is the grouping —CH= that is oxidized into the carboxyl group $-C\overset{O}{\underset{OH}{<}}$. If the carbon atom which has the double bond does not contain hydrogen, ketones are formed as a result of oxidation (reaction 3).

Catalytic oxidation by the oxygen of the air causes the formation of *α-oxides of olefins*, which are of great importance in organic synthesis. For example, a very important industrial product, *ethylene oxide*, is obtained:

$$CH_2=CH_2+O_2 \xrightarrow{Ag;\ heat} \underset{\displaystyle O}{H_2C-CH_2}$$

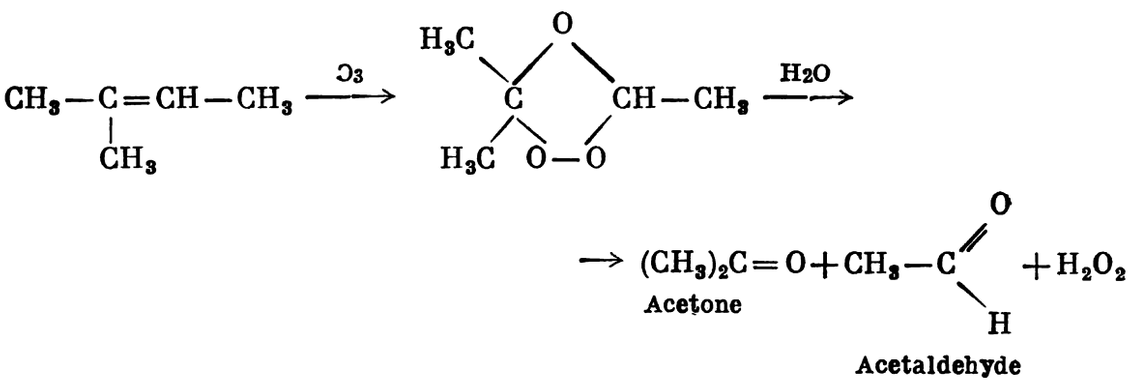
Ozonization or ozonolysis. Olefins readily react with ozone, forming addition products, i.e., cyclic peroxides known as *ozonides*:



Ozonide

Ozonides are viscous liquids or solids. They are very unstable and explosive. They are not usually isolated, but are decomposed by water as soon as they are formed. In this case, carbonyl compounds (aldehydes and ketones) are formed; their structure indicates the structure of the olefin which was subjected to ozonolysis. Hydrogen peroxide, which can react with aldehydes and ketones, is formed as by-product at the expense of oxygen of the peroxide bridge; to prevent its formation, hydrolysis is carried out in the presence of a reducing agent (zinc dust).

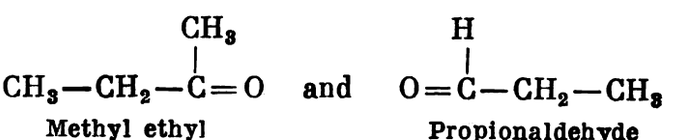
For example, when 2-methyl-2-butene is ozonized, first its ozonide is formed, and then ketone and aldehyde are formed on decomposition by water and zinc dust:



Acetone

Acetaldehyde

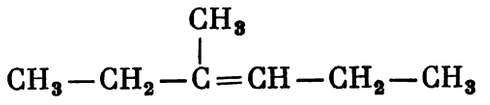
The formal result of ozonolysis with the subsequent action of water is the breakdown of the olefin molecule across the double bond and the addition of the oxygen atom to the valencies which have become free in each of the fragments. To determine the olefin structure by the ozonization products, let us imagine that oxygen is removed from them and the fragments obtained are linked by a double bond. For example, if the following compounds were obtained in ozonolysis:



Methyl ethyl ketone

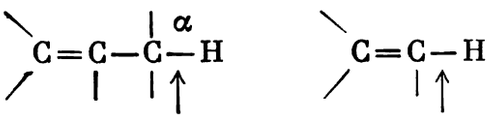
Propionaldehyde (propanal)

the initial olefin had the following structure:



3-Methyl-3-hexene

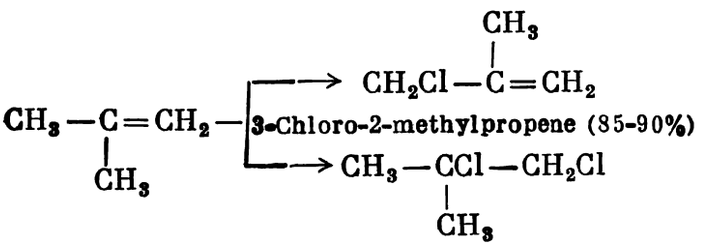
Substitution reactions. In some cases, olefins can undergo also substitution reactions. Hydrogen at the α-hydrogen atom relative to the double bond (the allylic position) is substituted most readily:



Bond energy 322 kJ/mole

Bond energy 435 kJ/mole

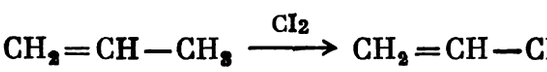
For example, under the action of chlorine, isobutylene turns into a dichlorinated compound only to a small degree, while an unsaturated compound is the principal product:



3-Chloro-2-methylpropene (85-90%)

1,2-Dichloro-2-methylpropane (10-15%)

The nearest homologue of ethylene, propylene, forms allyl chloride by chlorination in a gaseous phase (500°C):



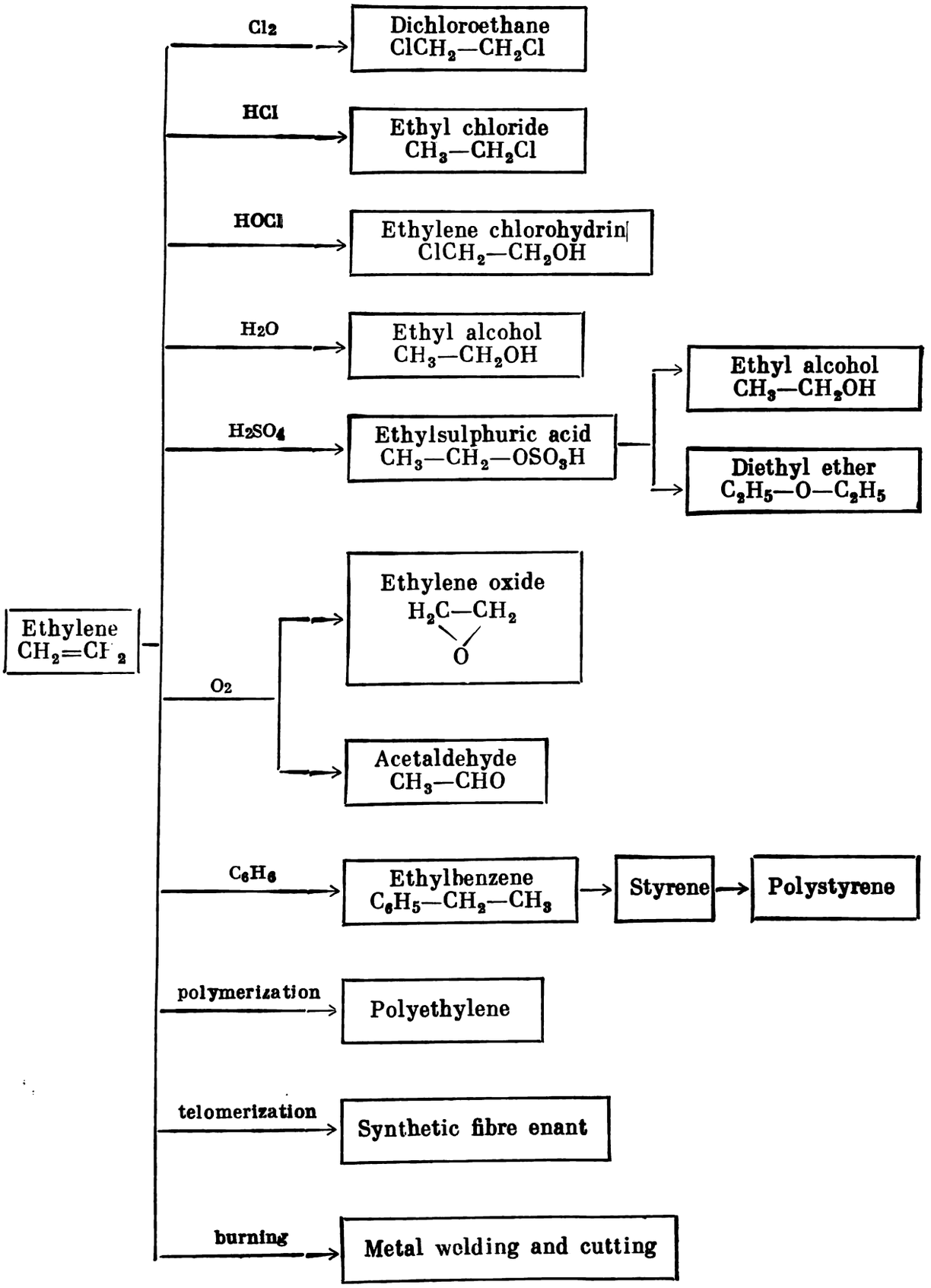
This reaction is part of an important process, i.e., the synthesis of triatomic alcohol, glycerol, $CH_2OH—CHOH—CH_2OH$, from petroleum raw material.

The substitution reactions which we have discussed are practically important; moreover, they are interesting theoretically, showing that the concept of the complete similarity of the chemical properties of homologues is correct only in the first approximation.

As we can see from the chemical characteristics, alkenes considerably differ from isomeric cycloalkanes (see Sec. 3.4).

4.6. Important Individual Alkenes. *Ethylene*, C_2H_4, is a gas; it dissolves poorly in water (its dissolution capacity is 0.25 part per part of water at 0°C), and better in alcohol (3.6 parts); when it burns, its flame is brighter than that of methane, because its carbon content is greater. The mixture of ethylene and air is explosive. Ethylene is formed in the dry distillation of organic substances, and it is always contained in illuminating gas. The main industrial sources of ethyl-

DIAGRAM 4.1. Industrial Use of Ethylene



ene are gas from petroleum cracking and coal gas. The latter contains a considerable amount of ethane, whose dehydrogenation produces ethylene.

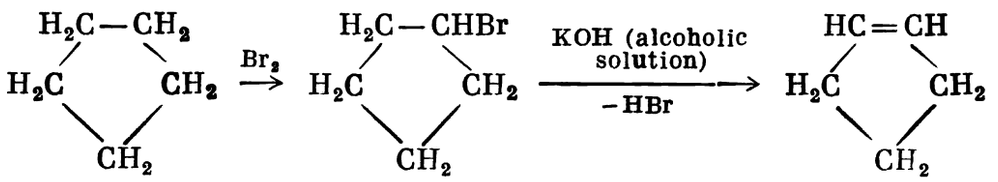
Ethylene is one of the most important intermediates for the organic synthesis industry. Many substances obtained directly from ethylene by chlorination, hydrochlorination, hydration and oxidation are used in practice, and they are also employed for further syntheses. The most important ways in which ethylene is used industrially are given in Diagram 4.1 on p. 94.

Propylene, C_3H_6, is a gas; it is obtained industrially from the gases from the cracking of petroleum or from oil gas (by the dehydrogenation of propane). It is an intermediate for synthesizing isopropyl alcohol, acetone, allyl chloride, glycerol, polypropylene, etc.

Isobutylene, C_4H_8, is a gas; it is contained in the butane-butylene fraction of gases from petroleum cracking from which it is isolated. It is used for synthesizing isooctane (see Sec. 4.5), for obtaining polyisobutylene, etc.

Butylenes (1-butene and 2-butene) are gases; they are isolated from the butane-butylene fraction of gases from cracking of petroleum. Butadiene (divinyl) is obtained in the catalytic dehydrogenation of butylenes; it is an important product for obtaining synthetic rubber.

Cyclopentene, C_5H_8, is a liquid whose boiling point is 44°C. It can be obtained from cyclopentane:



Chapter 5

ALKYNES

Alkynes are unsaturated hydrocarbons which contain one triple bond in the molecule. The simplest alkyne is acetylene C_2H_2, and therefore they are often called *acetylene hydrocarbons*. The general formula of alkynes is C_nH_{2n-2}, i.e., the molecule has four hydrogen atoms less than the corresponding alkanes, and two hydrogen atoms less than the corresponding alkenes. The nearest homologues of acetylene are the hydrocarbons C_3H_4, C_4H_6, C_5H_8, etc.

5.1. Structure of Alkynes. Isomerism. Nomenclature. Structure. The main factor which characterizes the essence of alkynes is the *triple* carbon-carbon bond —C≡C—.

Three pairs of shared electrons participate in the formation of the triple bond (*six-electron bond*). Carbon atoms which form the

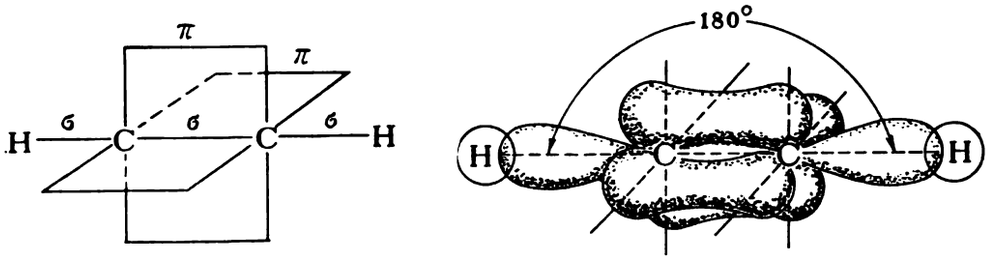


Fig. 5.1. Structure of acetylene

triple bond are in the state of *sp* hybridization. Each of them forms *two* σ-bonds, which are at an angle of 180°. Two unhybridized *p*-orbitals of each carbon atom are arranged at a right angle (90°) relative to one another and parallel to the corresponding orbitals of another atom. They overlap in pairs, forming two π-bonds, which are arranged in two mutually perpendicular directions. The triple bond is a combination of one σ- and two π-bonds. Figure 5.1 illustrates the arrangement of bonds in the acetylene molecule. In the formation of the triple bond, carbon atoms approach one another even closer than in the formation of the double bond: the length of the triple carbon-carbon bond is 0.120 nm.

In the state of sp^3, sp^2 and *sp* hybridizations of carbon atoms, the portion of the *s*-component in the hybridized orbitals is different

(1/4, 1/3 and 1/2, respectively). The greater the portion of the *s*-orbital in the hybrid state, the closer are the bonding electrons to the nuclei of the bonded atoms and the shorter is the bond, because the spherical *s*-component is capable of retaining the electrons at the nucleus to a greater extent than the *p*-component. In the series $sp^3 \rightarrow sp^2 \rightarrow sp$, the covalent radius of carbon diminishes (0.077, 0.067 and 0.060 nm).

Isomerism. The isomerism of alkynes is caused by the branching of the carbon chain and the position of the triple bond; they are similar to alkenes in this respect. But *cis*-, *trans*-isomers cannot exist in acetylene hydrocarbons, because the two σ-bonds formed by the carbon atom in the state of *sp* hybridization are at an angle of 180°, i.e., they lie on the single line. All the four atoms which constitute acetylene are on the same straight line, and the molecule is ***linear.***

Nomenclature. The principle of naming alkynes is the same as that for alkenes. By rational nomenclature, an alkyne compound is an acetylene derivative, and by modern substitutive nomenclature alkyne names end with **yne.** In naming alkynes, the selection of the principal chain and the beginning of numeration are determined by the triple bond. Several examples of compounds and their rational names are given below; the names in parentheses are those of modern substitutive nomenclature:

$CH_3-CH_2-C\equiv CH$
Ethylacetylene (1-butyne)

$CH_3-C\equiv C-CH_3$
Dimethylacetylene (2-butyne)

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C\equiv CH$$
Isobutylacetylene (4-methyl-1-pentyne)

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-CH_3$$
Methylisopropylacetylene (4-methyl-2-pentyne)

If a molecule simultaneously has triple and double bonds, the numbering of the double bond has precedence over the triple bond:

$CH_2=CH-CH_2-CH_2-C\equiv CH$
1-Hexene-5-yne

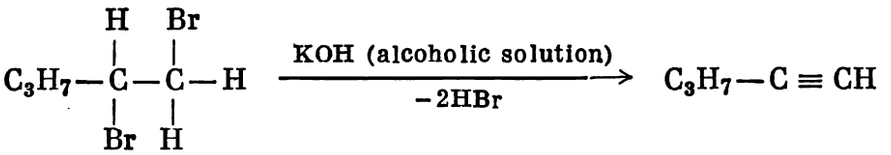
The alkyne radicals found most frequently are:

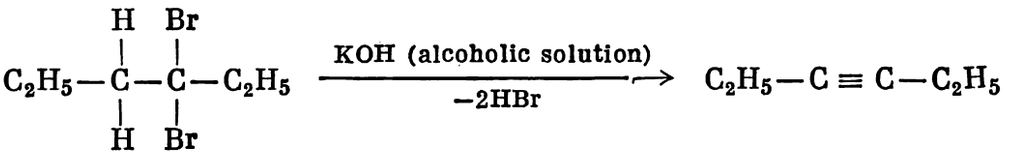
$CH\equiv C-$, **ethynyl;** $CH\equiv C-CH_2-$, **propargyl**

5.2. Preparation of Alkynes. Alkynes can be obtained by the following reactions:

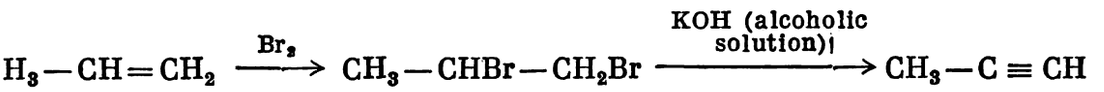
1. From the dihaloalkanes by eliminating a hydrogen halide under the action of an alcoholic solution of potassium hydroxide or sodium amide.

The initial dihalides can have halogen atoms attached to the adjacent carbon atoms or to one carbon atom:





Dihalides, which contain halogen atoms attached to the adjacent carbon atoms, are usually obtained by the addition of a halogen to olefins, and therefore this method is of particular importance, because it allows us to turn alkenes into alkynes:



2. From alkyl halides and acetylides of sodium or magnesium:

$$CH \equiv CNa + CH_3I \rightarrow CH \equiv C-CH_3 + NaI$$

$$CH \equiv CMgBr + BrC_2H_5 \rightarrow CH \equiv C-C_2H_5 + MgBr_2$$

This reaction makes it possible to convert simple alkynes into complex ones.

Compounds containing several triple bonds in a molecule have been found in Compositae and Umbelliferae. For example, yellow hydrocarbon, called 1-tridecene-3,5,7,9,11-pentayne, has been extracted from sunflower:

$$CH_3-C \equiv C-C \equiv C-C \equiv C-C \equiv C-C \equiv C-CH=CH_2$$

Preparation of acetylene. The most important alkyne, *acetylene*, is obtained industrially in large amounts. The raw-material sources of acetylene are coal, natural gas and petroleum.

Coal is turned into calcium carbide by heating it in a mixture with lime in electric furnaces:

$$3C + CaO \xrightarrow{2000°C} CaC_2 + CO$$

Water decomposes calcium carbide with the formation of acetylene:

$$CaC_2 + 2H_2O \rightarrow CH \equiv CH + Ca(OH)_2$$

This method is used both in the laboratory and in industry, where it has been mastered as early as the nineteenth century. Carbide acetylene served as raw material for the organic synthesis industry in coal-rich countries (Germany, England). But high energy consump-

tion is required to obtain it, and therefore carbide acetylene is expensive.

In a more modern method, the initial material is methane, which is turned into acetylene by *thermal cracking* or *electrocracking*:

$$2CH_4 \xrightarrow{1500°C} C_2H_2 + 3H_2$$

Another way is *oxidative pyrolysis*, or the burning of methane with a limited amount of air. In this case, methane is partially oxidized with the formation of hydrogen and carbon monoxide. The heat of reaction creates the temperature which is needed for decomposing methane:

$$6CH_4 + O_2 \xrightarrow{1500°C} 2CH \equiv CH + 2CO + 10H_2$$

Hydrogen and carbon monoxide are used for obtaining alcohols.

Acetylene is formed from methane homologues at a lower temperature:

$$C_2H_6 \xrightarrow{1200°C} C_2H_2 + 2H_2 \quad 2C_3H_8 \longrightarrow 3C_2H_2 + 5H_2$$

Natural gas or petroleum serves as raw material in these methods. Acetylene thus produced is cheaper than carbide acetylene, but its purification is complicated and is still a problem.

Acetylene can be obtained by direct synthesis from elements (Berthelot, 1862) when hydrogen is passed into the flame of an electric arc between carbon electrodes:

$$2C + H_2 \longrightarrow C_2H_2$$

This technique is of no practical importance. Acetylene is formed in the dry distillation of many organic substances, and it is always contained in the illuminating gas of pit-coal origin (coke gas).

5.3. General Characteristics of Physical and Chemical Properties. Physical properties. Alkynes are similar to olefins and paraffins by their physical properties. Lower alkynes C_2-C_4 are gases, C_5-C_{16} are liquids, and higher alkynes are solids. The boiling points and densities of alkynes are somewhat higher than those of the corresponding alkenes. For example, ethylene boils at —103°C, acetylene, at —83.6°C, and propylene and methylacetylene, at —47°C and —23°C, respectively.

The water-solubility of lower alkynes is somewhat higher than that of alkenes and alkanes, but it is still very poor.

Chemical properties. The chemical properties of acetylene hydrocarbons are determined by the nature of the triple bond and the specific features of carbon atoms in the state of *sp* hybridization.

The energy of formation of the triple bond ($\sigma + 2\pi$) is 810 kJ/mole. The difference in the energies of formation of acetylene and ethylene is 190 kJ/mole, and this is less than the difference in the energies of

formation of ethylene and ethane (ca. 270 kJ/mole). *Addition reactions* are typical of acetylene and its homologues as unsaturated compounds.

Many alkyne reactions are electrophilic addition ones which occur similarly to the corresponding olefin reactions, but at two consecutive stages. At first, addition occurs along the triple bond with the formation of olefin derivatives, and then along the double bond with the formation of paraffin derivatives.

The reaction mechanism, exemplified by the reaction between acetylene and hydrogen bromide, can be illustrated by the scheme:

$$CH \equiv CH \xrightarrow{H^+} CH=\overset{+}{C}-H \xrightarrow{Br^-} CH=C(H)(Br)$$

$$CH_2=CHBr \xrightarrow{H^+} CH_3-\overset{+}{C}HBr \xrightarrow{Br^-} CH_3-CHBr_2$$

Alkynes are unsaturated more than alkenes, and therefore it seems that they should react more readily with electrophiles. But since the π-electrons of the triple bond are concentrated at the nuclei of carbon atoms and are less susceptible to attack by reagents, electrophilic reactions typical of acetylene hydrocarbons occur more slowly than those typical of olefins.

The triple bond is oxidized with greater difficulty than the double bond, and therefore the double bond can be selectively oxidized in the presence of the triple bond. The same oxidizing reagents can be used, but the conditions are more rigid.

The triple bond is thermally more stable than the single bond, as is confirmed by obtaining acetylene from methane and its homologues in thermal cracking (1200-1500°C) (see Sec. 5.2).

When the portion of the *s*-component in the hybrid *sp*-orbital increases, the polarity of the C—H bond grows, because the electronegativity of the carbon atom then becomes greater:

Hybridization	Portion of the *s*-orbital	Relative electronegativity
sp^3	1/4	2.50
sp^2	1/3	2.62
sp	1/2	2.75

Strong polarization of the C—H bond in the acetylene molecule makes acetylene acidic. The homolytic cleavage of the bond with the formation of radicals is hindered, while heterolytic cleavage occurs more readily:

$$CH \equiv C : H \longrightarrow CH \equiv \overset{-}{C} : + H^+$$

Acetylene, unlike ethane and ethylene, is capable of giving metallic derivatives: acetylides.

Acetylene can undergo reactions also with nucleophilic reagents, although they occur more slowly than those with electrophiles.

An example is the reaction with hydrogen cyanide HCN:

$$CH \equiv CH \xrightarrow{-CN^-} CH=CH-CN \xrightarrow{H^+} \underset{\text{Acrylonitrile}}{CH_2=CH-CN}$$

5.4. Reactions of Alkynes. Addition reactions. 1. Halogen addition. Alkynes are less reactive to halogenation than alkenes are. A rapid colour change of bromine water is a qualitative reaction for the multiple bond:

$$CH \equiv CH + Br_2 \longrightarrow \underset{\text{1,2-Dibromoethylene}}{BrCH=CHBr}$$

$$BrCH=CHBr + Br_2 \longrightarrow \underset{\text{1,1,2,2-Tetrabromoethane}}{Br_2CH-CHBr_2}$$

1,2-Dichloroethylene, ClCH=CHCl, and then 1,1,2,2-tetrachloroethane, $Cl_2CH-CHCl_2$, are formed under the action of chlorine.

2. Addition of hydrogen halides. Hydrogen halides are added to the triple bond with greater difficulty than to the double bond:

$$CH \equiv CH + HF \longrightarrow \underset{\substack{\text{Vinyl}\\\text{fluoride}}}{CH_2=CHF}$$

$$CH_2=CHF + HF \longrightarrow \underset{\text{1,1-Difluoroethane}}{CH_3-CHF_2}$$

The reaction is of particular importance in obtaining vinyl chloride.

The alkyl-substituted acetylenes R—C≡CH add hydrogen halide according to Markovnikov's rule:

$$RC \equiv CH \xrightarrow{HBr} RBrC=CH_2 \xrightarrow{HBr} RBr_2C-CH_3$$

3. Hydrogenation. The triple bond hydrogenates more readily than the double bond:

$$CH \equiv CH + H_2 \longrightarrow CH_2=CH_2$$

$$CH_2=CH_2 + H_2 \longrightarrow CH_3-CH_3$$

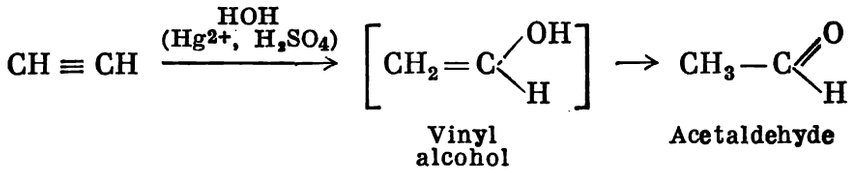
The reaction can be stopped at the olefin.

To hydrogenate the triple bond, use can be made of nascent hydrogen (lithium or sodium in liquid ammonia). It is possible to use also hydrogenation by molecular hydrogen over the palladium catalyst on calcium carbonate or Raney nickel. Alkenes are not hydrogenated under these conditions.

4. Hydration (water addition). The reaction occurs more readily than for alkenes. The catalyst in this case is dilute sulphuric acid and mercuric salts. This reaction was discovered by M. G. Kucherov (1881).

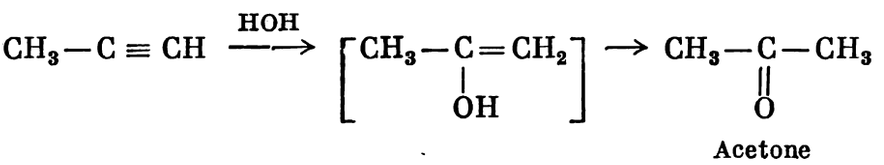
At first, an unstable product with a hydroxyl attached to the carbon, which is linked by a double bond (see Eltekov's rule, Sec. 10.5),

is formed, and then it isomerizes into acetaldehyde:

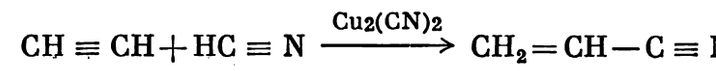


Kucherov's reaction is of great industrial importance in acetaldehyde synthesis, which is widely used for preparing acetic acid, ethyl alcohol and other products of organic synthesis.

The homologues of acetylene are hydrated more readily than acetylene. The reaction occurs according to Markovnikov's rule, as a result of which ketones are formed:



5. Addition of hydrogen cyanide. This method is used industrially for obtaining an important product, acrylonitrile:

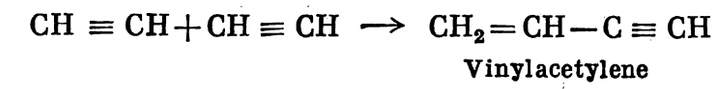


Reactions of addition of organic compounds, such as alcohols, carboxylic acids, aldehydes and ketones, to acetylene are of great importance.

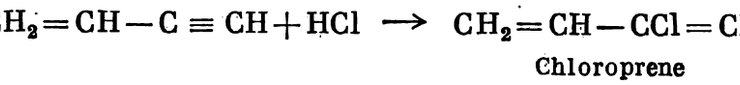
Oxidation. Alkynes are oxidized readily, and the process is often accompanied by a cleavage of the carbon chain at the site of the triple bond. When a potassium permanganate solution is added, alkynes rapidly decolorize it, and this can be used as a qualitative reaction for the triple bond.

Polymerization reactions. Alkyne molecules can react with one another under the action of catalysts, and different products are formed, depending on the conditions.

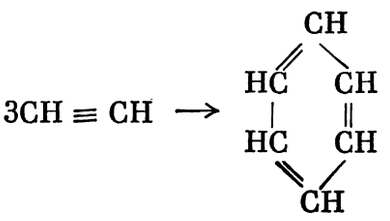
(a) Dimerization of acetylene under the action of an aqueous solution of cuprous and ammonium chlorides:



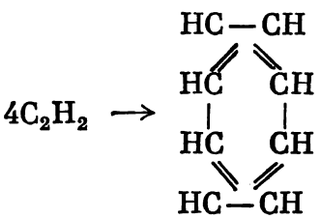
Vinylacetylene has great reactivity; when it adds hydrogen chloride, it forms chloroprene, which is used for preparing synthetic rubber (see Sec. 23.5).



(b) Benzene is formed when acetylene is passed over activated charcoal at 600°C (N. D. Zelinsky, B. A. Kazansky):



At present, a similar reaction involving complex metallic catalysts is used for synthesizing a compound having an eight-membered unsaturated ring, known as *cyclooctatetraene*:



Hydrogen substitution reactions. The hydrogen atom in the acetylene molecule and in monoalkyl derivatives R—C≡CH is capable of being replaced by metal.

Hydrogen is replaced by alkali metal and acetylide is formed under the action of strong bases, such as alkali metal amides in liquid ammonia:

$$R-C\equiv \overset{\delta-}{C}-\overset{\delta+}{H}+NaNH_2 \longrightarrow R-C\equiv C-Na+NH_3$$

Alkyne acts as an acid in this case and gives away a proton to a strong base. *Acetylides* are salt-like products, readily hydrolyzable by water. Acidic properties are expressed more poorly in acetylene than in water.

Magnesium acetylides (obtained for the first time by Iotsich in 1902) are formed under the action of organomagnesium compounds:

$$R-C\equiv C-H+CH_3MgI \longrightarrow R-C\equiv C-MgI+CH_4$$

Acetylides of sodium and magnesium are used in various syntheses. Calcium carbide, mentioned earlier, is also acetylide by its structure (calcium acetylide).

A qualitative reaction for the hydrogen atom on a triply bonded carbon is the formation of a silver acetylide and also a cuprous acetylide. When acetylene (and hydrocarbons of the R—C≡CH type) is passed through ammoniacal solutions of silver nitrate or cuprous chloride, characteristic precipitates are formed: AgC≡CAg of white colour and CuC≡CCu of reddish brown colour. They are explosive when dry.

The ammoniacal solution of silver nitrate contains complex silver ammoniate $[Ag(NH_3)_2]OH$, which reacts with acetylene:

$$CH \equiv CH + 2[Ag(NH_3)_2]OH \longrightarrow AgC \equiv CAg + 4NH_3 + 2H_2O$$

Similarly, the ammoniacal solution of cuprous chloride contains complex copper ammoniate $[Cu(NH_3)_2]OH$.

This reaction can be used for isolating acetylene hydrocarbons from mixtures. After precipitating and separating acetylides, free alkynes can be regenerated under the action of mineral acids:

$$AgC \equiv CAg + 2HCl \longrightarrow CH \equiv CH + 2AgCl$$

5.5. Acetylene, Its Properties and Application. Acetylene is odourless in pure form. The repugnant odour of acetylene which is obtained from calcium carbide is due to the impurities of hydrogen sulphide and phosphine.

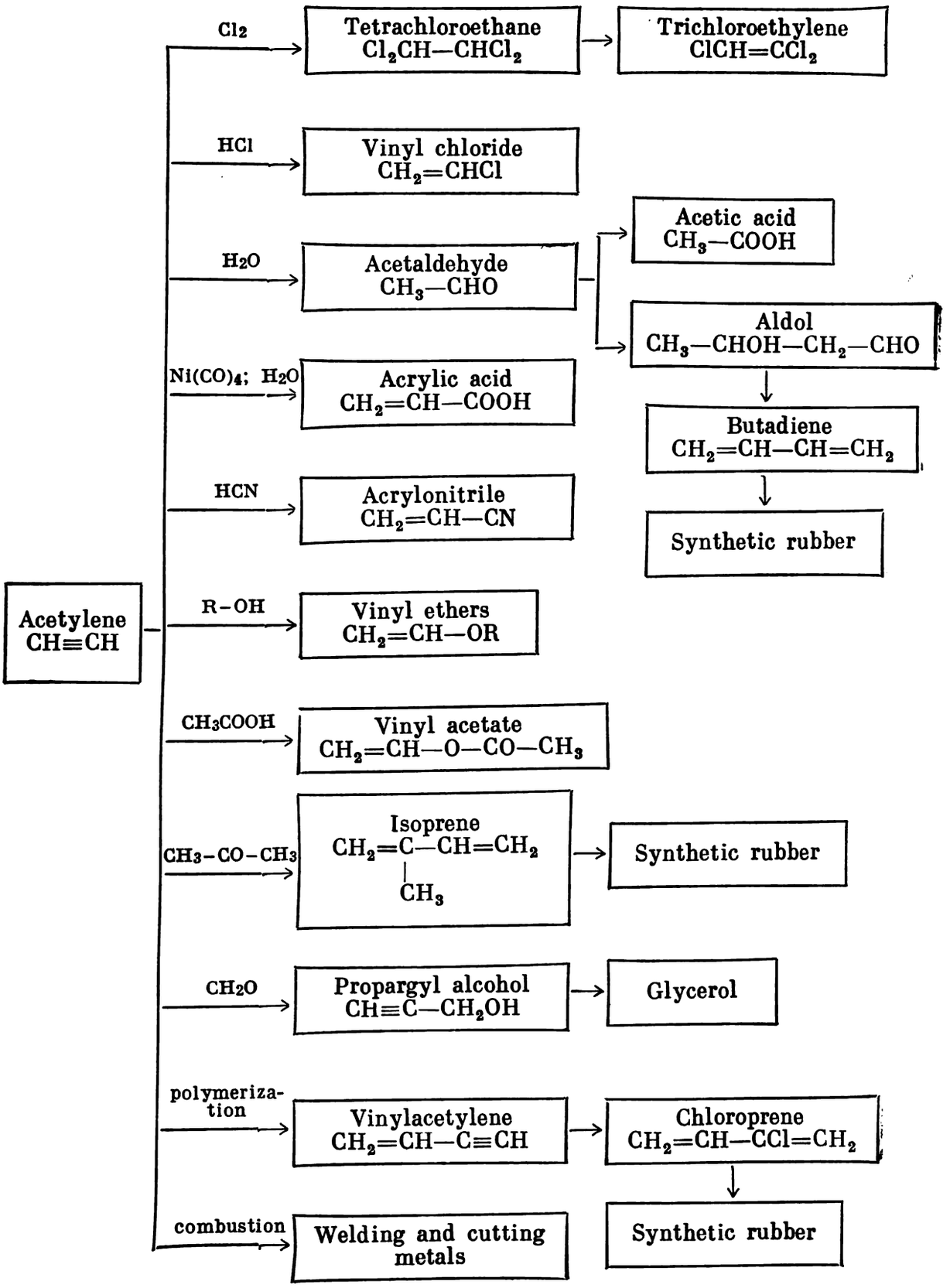
Acetylene dissolves in an equal amount of water under ordinary conditions, but its solubility increases as pressure rises. A mixture of acetylene and air is explosive within a wide range of acetylene concentrations, i.e., from 3 per cent to 82 per cent, and therefore great care must be taken when acetylene is used. Acetylene is preserved as a solution in acetone (one part of acetone dissolves 25 parts of acetylene at standard pressure and 300 parts at a pressure of 12-15 kg/cm^2) under pressure in steel cylinders which contain porous material: either asbestos or kieselguhr.

Acetylene is an endothermic compound, and a large amount of energy is required for its formation; much heat is evolved (1300 kJ/mole) when it is burned. The temperature of the oxygen-acetylene flame is ça. 3000°C, i.e., it is higher than the combustion temperature of ethylene and ethane. At this temperature, a part of acetylene decomposes into elements, forming minute brightly scintillating particles. In the nineteenth century, carbide lanterns were used for illuminating streets and squares. Acetylene was used also for the lanterns of carriages and bicycles. Oxygen-acetylene burners are now employed for welding and cutting metals. The acetylene flame smokes greatly when there is not enough oxygen.

Many branches of the organic synthesis industry developed on the basis of acetylene.

Investigations by Soviet scientists are of great importance in the development of the chemistry of acetylene. In this respect, a prominent role had been played by A. Ye. Favorsky (1860-1945) and his school: they worked out a new method (which does not involve the use of mercury) of obtaining acetaldehyde and new ways of obtaining high-molecular-weight compounds: synthetic rubber, plastics, general-purpose glue (Nazarov's glue) and medicinals (Shostakovsky's balsam).

DIAGRAM 5.1. Industrial Use of Acetylene



Reactions between acetylene and acetylene hydrocarbons, on the one hand, and ketones, on the other, are of great interest. For example, the reaction between acetylene and acetone can be used for obtaining isoprene, which is the initial product for producing synthetic rubber.

Diagram 5.1 gives the most important industrial acetylene-based syntheses. Some of them will be understood completely after the student becomes acquainted with other classes of organic compounds.

It should be noted that a number of chemical products obtained from acetylene can be synthesized also from ethylene, and this is often more economical.

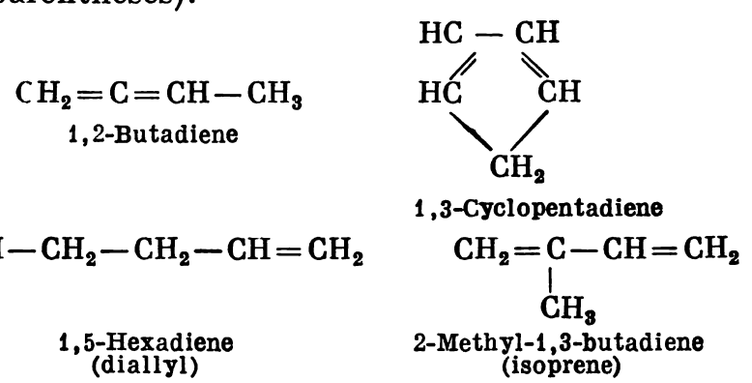
Chapter 6

DIENE HYDROCARBONS

Compounds containing two double bonds in the carbon chain are known as diene compounds. Hydrocarbons of such a type with an open chain are called alkadienes, while cyclic ones, cycloalkadienes.

6.1. Isomerism. Nomenclature and Classification. The general formula of alkadienes is C_nH_{2n-2} (like that of acetylenes). It follows that compounds having two double bonds are isomeric relative to compounds having one triple bond.

The isomerism of diene compounds is, in turn, determined by the structure of the carbon skeleton and the relative arrangement of the double bonds. In names, the position of every double bond is denoted by figures. The letters **di**, meaning "two" in Greek, are prefixed to the ending **ene**, which symbolizes the double bond, and this is how the ending **diene** is formed. Many diene hydrocarbons also have trivial names. Several examples are given below (trivial names are in parentheses):



The presence of two double bonds in the molecule and their relative arrangement affect, as a result of their mutual influence, the properties of compounds. This influence is especially strong when the double bonds are close to one another.

A distinction is made between the following diene hydrocarbons by the mutual arrangement of the double bonds.

Dienes with cumulated double bonds contain double bonds which are directly adjacent to one another (position 1,2):

Compounds of this type are unstable and have been studied inconsiderably.

Dienes with conjugated double bonds have double bonds in the position 1,3:

$$\underset{\text{Conjugated double bonds}}{C=C-C=C} \qquad \underset{\text{1,3-Butadiene (divinyl)}}{CH_2=CH-CH=CH_2}$$

Dienes with isolated double bonds have double bonds which are separated by one or more carbon atoms:

$$\underset{\text{Isolated double bonds}}{C=C-(C_n)-C=C} \qquad \underset{\text{1,4-Pentadiene}}{CH_2=CH-CH_2-CH=CH_2}$$

Compounds with isolated double bonds do not differ from alkenes by their chemical properties. Their addition reactions occur in the same way as the olefin ones, but two reagent molecules can enter into

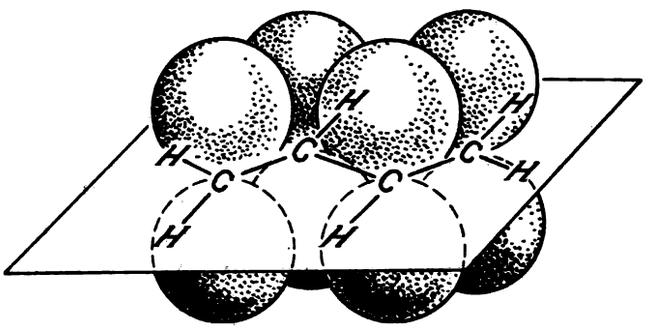


Fig. 6.1. Structure of butadiene

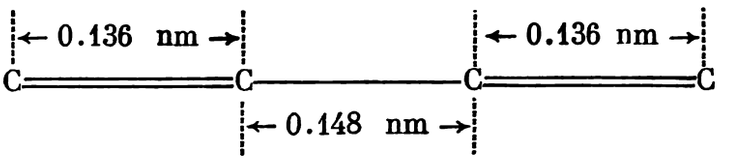
the reaction. In such compounds, double bonds react independently of one another, and therefore they are said to be isolated.

6.2. Compounds with Conjugated Double Bonds. Nature of conjugated double bonds. A typical example of compounds having conjugated double bonds is 1,3-butadiene $CH_2=CH-CH=CH_2$. In the butadiene molecule, all the carbon atoms are in the state of sp^2 hybridization, being on the same plane. The molecular orbital consists of four mutually parallel orbitals of π-electrons, which are perpendicular to the plane where carbon atom nuclei lie (Fig. 6.1).

When the mobile π-electron clouds of two conjugated bonds interact, a single π-electron cloud covering all the four carbon atoms originates. Lone π-electrons are not attached pairwise in definite bonds, but are delocalized, i.e., they are distributed along the entire conjugated system, along all the conjugated bonds, both single and multiple. Maximum electron density is formed between the carbon atoms 1-2 and 3-4, and the smaller density, between the atoms 2 and 3 (see Fig. 6.1).

The mutual effect of conjugated bonds is exhibited in a certain equalization of internuclear distances. The central bond (between

multiple bonds) is shorter than the normal σ-bond, while multiple bonds are somewhat longer than a normal double bond (the length of a C—C bond is 0.154 nm, while that of a double bond 0.133 nm):



Thus, the three bonds linking four carbon atoms are neither truly single nor truly double.

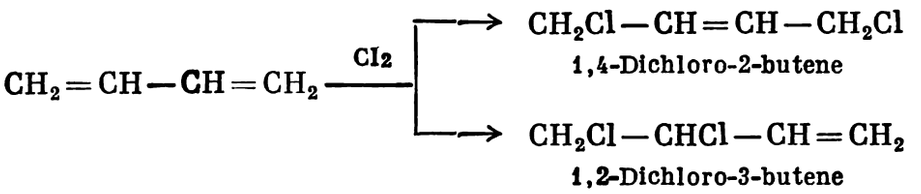
Conjugation causes a certain *double bonding* of carbon atoms, which are formally linked by the σ-bond (*non-integral multiple bond*).

Instead of using an ordinary formula, the butadiene can be shown more accurately when the distribution of π-electrons between all the C—C bonds is represented by the dotted lines:

$$CH_2{=}{=}CH{=}{=}CH{=}{=}CH_2$$

The amount of energy in a molecule diminishes when conjugated bonds are formed, and therefore *compounds having conjugated double bonds are the most stable ones among dienes.*

Chemical peculiarities of conjugated dienes. In the system of conjugated bonds, two unsaturated centres function as an entity. Addition to the system of conjugated double bonds can occur in two ways: towards the terminal positions of a system, i.e., positions 1 and 4 with the formation of a new double bond between atoms 2 and 3, or at the site of one of the double bonds, while the other bond remains unaffected. The first type is called 1,4-addition, and the second, 1,2-addition. For example, when chlorine is added to butadiene, two products are formed:



Let us consider the course of addition to the conjugated system by the interaction between butadiene and hydrogen chloride.

Like all the ordinary addition reactions to the double carbon-carbon bond, the process occurs by the electrophilic mechanism and begins with the proton addition at the expense of the π-electrons of the double bond (*first stage*). Addition proceeds according to Mar-

kovnikov's rule:

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2} \xrightarrow{H^+} \overset{1}{CH_3}-\underset{+}{\overset{2}{CH}}-\overset{3}{CH}=\overset{4}{CH_2}$$

In the carbonium ion formed, the positive charge is not concentrated on carbon C_2, because a double bond with its mobile π-electrons is next to the charge. The attraction of π-electrons results in their displacement towards the centre of the molecule, while the charge is transferred to the atom C_4, which had lost an electron in the migration of the double bond. This is how the carbonium ion $CH_3-CH=CH-\overset{+}{C}H_2$ originates. In it, however, the interaction between the positive charge and the π-electrons of the double bond should promote reconversion into the initial cation with a charge on the atom C_2. Apparently, the most stable state will be that which is intermediate between the extreme states expressed by both formulas. This is represented nominally, both formulas being written down and connected with a double-headed arrow:

$$CH_3-\overset{+}{C}H-CH=CH_2 \leftrightarrow CH_3-CH=CH-\overset{+}{C}H_2$$

Structures in which the true distribution of electrons is intermediate between those described by ordinary formulas are said to be *mesomeric*, while formulas which limit the mesomeric state are called *extreme formulas*.

To give a clearer picture of the intermediate nature of electron distribution, another form can be written:

$$\overset{1}{CH_3}-\underbrace{\overset{2}{CH}=\overset{3}{CH}=\overset{4}{CH_2}}_{+}$$

In the carbonium ion formed, the positive charge is not localized on a definite atom. Carbon atoms 2 and 4 are electron deficient and the chlorine ion can attack any of them (*second stage*):

$$CH_3-\overset{+}{C}H-CH=CH_2 \leftrightarrow CH_3-CH=CH-\overset{+}{C}H_2$$

$$\downarrow +Cl^- \qquad\qquad \downarrow +Cl^-$$

$$CH_3-CHCl-CH=CH_2 \qquad CH_3-CH=CH-CH_2Cl$$

1,2-Addition (about 80 per cent) — 1,4-Addition (about 20 per cent)

Addition reactions of other hydrogen halides, chlorine, bromine and hydrogen in catalytic hydrogenation occur similarly. The result (the direction in which a reaction is carried out) depends on the nature of a reagent and the reaction conditions. Several examples

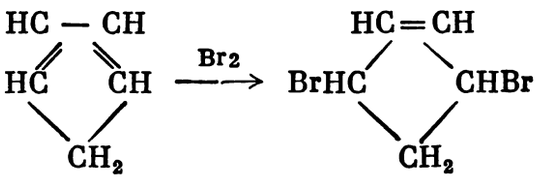
are given below:

$$CH_2=CH-CH=CH_2 \xrightarrow{Cl_2} \begin{cases} \longrightarrow CH_2Cl-CHCl-CH=CH_2 \ (50\%) \\ \longrightarrow CH_2Cl-CH=CH-CH_2Cl \ (50\%) \end{cases}$$

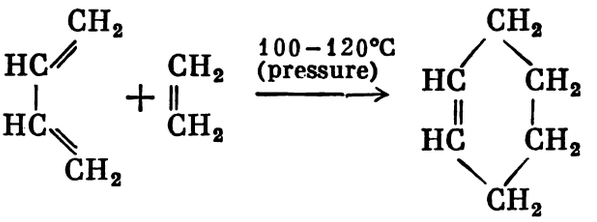
Hydrogen can be added to butadiene also in the positions 1,2 or 1,4, depending on the conditions:

$$CH_2=CH-CH=CH_2 \xrightarrow[C_2H_5OH+Na]{H_2/Pd} \begin{cases} \longrightarrow CH_3-CH_2-CH=CH_2 \\ \longrightarrow CH_3-CH=CH-CH_3 \end{cases}$$

A cyclic conjugated diene, cyclopentadiene, adds bromine only in the positions 1,4:

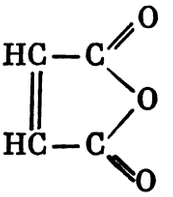


A very important reaction in synthetic chemistry is *diene synthesis*: 1,4-addition of alkene to conjugated systems (Diels-Alder reaction, 1928). Diene interacts with a compound containing an active double bond, a *dienophile*:



Cyclohexene

The cyclohexene yield is low. However, if the dienophile is not ethylene, but a compound which has groups that activate the double bond (nitrile, aldehyde, anhydride, etc.), the reaction occurs rapidly and under mild conditions. The reaction being considered is important not only in synthesizing six-membered rings, but also in identifying diene hydrocarbons. A characteristic dienophile, a reagent for the conjugated double bond, is *maleic anhydride*:



Compounds having conjugated double bonds tend to undergo *polymerization* reactions. An example is the polymerization of buta-

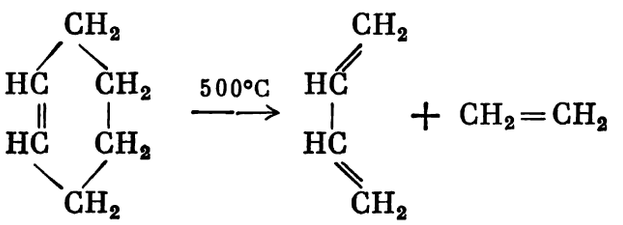
diene due to the 1,4-addition:

$$CH_2=CH-CH=CH_2+CH_2=CH-CH=CH_2+CH_2=CH-CH=CH_2+\ldots\rightarrow$$
$$\rightarrow\ldots-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-\ldots$$

Polymerization reactions are very important practically, being used for obtaining various types of synthetic rubber. The reaction of butadiene polymerization is dealt with in greater detail in Sec. 23.5.

6.3. Butadiene, Isoprene, Cyclopentadiene. 1,3-*Butadiene* (divinyl) is the first and most important representative of the homologous series of dienes. It is a readily liquefying gas (b.p. —4.5°C) which has a peculiar repugnant odour.

In the laboratory, it is convenient to obtain butadiene by Zelinsky's method, i.e., by passing cyclohexene vapours over red-hot wire:



This is in essence a reverse process in comparison with the diene synthesis considered above.

Butadiene is formed under the action of high temperatures and from many other hydrocarbons. Therefore, it is always contained in products which are obtained in the pyrolysis of oil.

Butadiene is obtained industrially in large amounts, because it is raw material for producing synthetic rubber. The following ways are used.

1. It is obtained from ethanol by the method proposed by S. V. Lebedev (1874-1934). The process consists in the simultaneous dehydrogenation, condensation and dehydration of alcohol, which are effected on a mixed catalyst (zinc and aluminium oxides with small additions of other substances):

$$2C_2H_5OH \xrightarrow{ZnO;\ Al_2O_3(400^\circ C)} CH_2=CH-CH=CH_2+2H_2O+H_2$$

This method was used to initiate the world's first large-scale production of synthetic rubber from butadiene in the Soviet Union in the early 1930's. Since alcohol for industrial purposes is now obtained from inedible raw material, the industrial synthesis of butadiene from alcohol has lost none of its importance even today, although there are other methods based on the use of the products of oil refining or coal conversion (acetylene).

2. By dehydrogenating butylenes (600°C, the catalyst is chromium oxide on alumina):

$$\left.\begin{array}{l} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{array}\right\} \xrightarrow{-2H} CH_2=CH-CH=CH_2$$

Raw material in this case is the butane-butylene fraction of gases from petroleum cracking and also the accompanying oil gas. Butane contained in this raw material dehydrogenates as well and produces butylenes:

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{-2H} \begin{cases} \longrightarrow CH_3-CH=CH-CH_3 \\ \longrightarrow CH_2=CH-CH_2-CH_3 \end{cases}$$

3. It is obtained from acetylene (in several ways), for example, through acetaldehyde:

Acetylene → Acetaldehyde → Aldol → Butylene glycol → Butadiene

4. Butadiene is extracted from the products of oil pyrolysis by special solvents, such as dimethylformamide

$$H-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$$

2-*Methyl*-1,3-*butadiene* (*isoprene*) is a liquid whose boiling point is 34°C. Isoprene itself is not found in nature, but compounds whose carbon skeleton is made out of isoprene units are widespread in the animal and vegetable kingdoms. They are known as *isoprenoids*. This type of compounds includes natural rubber, which is a polymer of isoprene units (see Sec. 23.5). Terpenes are also important isoprenoids (see Sec. 22.9).

Isoprene in pure form was obtained for the first time by heating natural rubber without aeration (dry distillation). At present, more than 20 methods of its synthesis are known, but only some of them became important industrially, such as:

1. Dehydrogenation of isopentane (550°C, reduced pressure):

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow{Cr_2O_3/Al_2O_3} CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2$$

Isopentane is isolated from oil fractions, and it is also obtained by catalytically isomerizing normal pentane.

2. Dimerization of propylene with the subsequent isomerization

and elimination of methane:

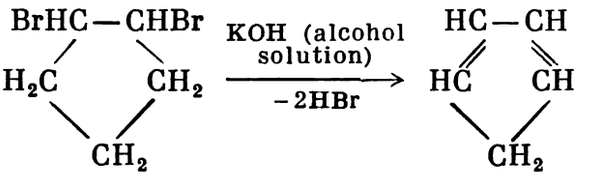
$$2CH_3-CH=CH_2 \xrightarrow{(C_3H_7)_3Al} CH_2=C(CH_3)-CH_2-CH_2-CH_3 \xrightarrow{SiO_2/Al_2O_3;\ 200^\circ C}$$

$$\rightarrow CH_3-C(CH_3)=CH-CH_2-CH_3 \xrightarrow{HBr;\ 750^\circ C} CH_2=C(CH_3)-CH=CH_2+CH_4$$

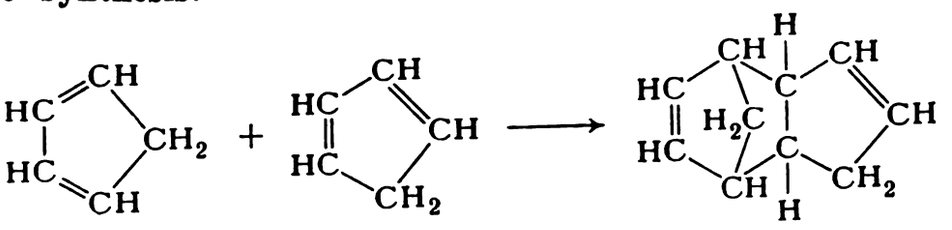
The first stage of this interesting synthesis, propylene dimerization, is similar to isobutylene dimerization considered earlier (see Sec. 4.5). In carrying it out, use is made of an organometallic catalyst, tripropyl aluminium $(C_3H_7)_3Al$; the second stage, the isomerization of the dimer over the catalyst, is accompanied by the shift of the double bond; the third stage, which is the most peculiar one, is effected by passing the product very rapidly (0.1 sec) through the heated region; the catalyst in this case is hydrogen bromide.

Methods of obtaining isoprene by condensing acetylene with acetone, and isobutylene with formaldehyde, are considered in the chapter on aldehydes and ketones.

1,3-*Cyclopentadiene* is a liquid whose boiling point is 42.5°C. It is formed when petroleum hydrocarbons are pyrolyzed and from the distillates produced in the carbonization of coal. It can be synthesized from 1,2-dibromocyclopentane by eliminating hydrogen bromide under the action of strong bases:



Cyclopentadiene is of great importance in synthetic chemistry. This substance polymerizes readily and is usually preserved as a dimer of higher stability. The reaction occurs according to the scheme of diene synthesis:



Dimer of cyclopentadiene

On heating, the dimer of cyclopentadiene splits into two monomeric molecules. A characteristic property of cyclopentadiene that distinguishes it from other compounds with double bonds is the acidic nature of the hydrogen atoms of the methylene group: these atoms are capable of being substituted for metal. Cyclopentadienyl sodium C_5H_5Na is formed when cyclopentadiene reacts with metallic sodium powder in boiling xylene.

Chapter 7

AROMATIC HYDROCARBONS

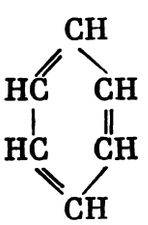
BENZENE AND ITS DERIVATIVES

At the beginning of the latter half of the nineteenth century, substances isolated from natural fragrant substances, such as plant resins, balsams, ladanum and essential oils, were said to be aromatic. These compounds were contrasted with aliphatic compounds, to which fats and other substances were referred. At present, the concept of aromaticity in the chemical sense does not relate in any way to odour. Aromatic substances are those whose molecules have a stable cyclic grouping with a special bond. The chemistry of aromatic compounds is above all that of benzene and its derivatives, and also the derivatives of naphthalene, anthracene, etc.

Many scientists studied aromatic compounds because of their specific chemical properties, and also because of their plentitude and significance. The revelation of the nature of aromaticity was very conducive to the development of theoretical and applied chemistry.

7.1. Benzene Structure. Nature of the Aromatic State. Benzene structure. Benzene, C_6H_6, the simplest member of aromatic hydrocarbons, was discovered by Faraday in illuminating gas in 1825. In 1845, Hofmann isolated it from coal tar.

Benzene, a substance of simple composition, has probably aroused the researchers' greatest interest. Among the numerous structural formulas proposed for benzene in the 1860's, the most successful was Kekulé's formula (1865), according to which benzene is 1,3,5-cyclohexatriene, a six-membered cyclic hydrocarbon with three conjugated double bonds:



Such a structure correctly reflected the equivalence of all the six hydrogen atoms of benzene and some other peculiarities of this substance. But Kekulé's formula could not explain why benzene does not have the properties of an unsaturated hydrocarbon.

Benzene does not produce reactions characteristic of unsaturated compounds: it does not decolorize bromine water and the alkaline solution of potassium permanganate. Instead, the hydrogen substitution reaction occurs under the action of bromine; the reaction is characteristic of saturated compounds, and it results in the formation of bromobenzene C_6H_5Br. Under the action of nitric acid, hydrogen is replaced by the nitro group, and nitrobenzene $C_6H_5NO_2$ is then formed.

Nevertheless, addition reactions can occur under definite conditions. In catalytic hydrogenation, the benzene molecule adds six hydrogen atoms, forming cyclohexane:

$$C_6H_6 \xrightarrow{H_2/Pt} C_6H_{12}$$

When benzene is exposed to intense light, it adds six chlorine atoms, forming hexachlorocyclohexane $C_6H_6Cl_6$. Benzene reacts also with ozone, producing unstable triozonide.

It follows from the given examples that benzene can exhibit unsaturation, but this property is expressed feebly under ordinary conditions. The thermal stability of benzene (up to 900°C) and its derivatives, the readiness of their formation, and the specific effect of the aromatic nucleus on the properties of the substituents linked with it are characteristic of benzene.

Only the development of electronic and quantum-mechanical concepts of chemical bonds made it possible to explain the specific features of aromatic compounds.

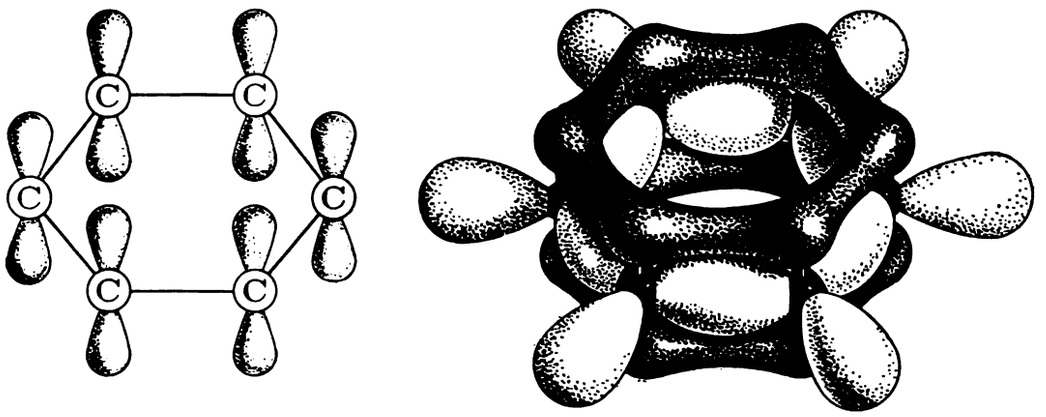
The energy of the benzene molecule can be determined by different methods. They all show that the real benzene molecule possesses less energy than when it were cyclohexatriene (Kekulé's formula), where electrons are fixed in double and single bonds. The heat of combustion calculated for the cyclohexatriene formula is 3453 kJ/mole, while that found experimentally for benzene is 3303 kJ/mole, being 150 kJ/mole less.

An isolated double bond in cyclohexene, or a double bond of alkene, is hydrogenated with the liberation of energy. But the hydrogenation of benzene requires energy consumption. The carbon-carbon bonds in the benzene molecule are distinguished by their strength, and much energy must be consumed to rupture them. The benzene molecule is stabilized, and the measure of its stability is *conjugation energy*. It is determined by various methods, being about 150 kJ/mole. The formation of aromatic compounds from nonaromatic ones is accompanied by the liberation of energy.

Nature of the aromatic state. Benzene is the most vivid example of a substance in which electrons are delocalized.

In the benzene molecule, all the carbon-carbon bonds are equalized, the length of all the bonds being the same (0.139 nm). It is

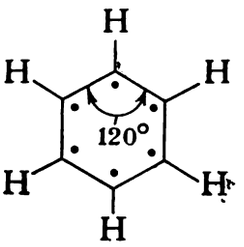
a planar molecule where six carbon atoms are arranged in the form of a regular hexagon. All the carbon atoms in the benzene ring are in the state of sp^2 hybridization. Each of them forms three ordinary σ-bonds (two C—C bonds and one C—H bond) at an angle of 120° between them, spending three valence electrons on this; the fourth electron of each carbon atom is not fixed. The orbitals of all the six *p*-electrons are perpendicular to the plane of the ring and mutually parallel (Fig. 7.1*a*). Each of the *p*-electrons of the given carbon



a *b*

Fig. 7.1. Model of σ- and π-bonds in benzene:
a—σ-bonds and individual π-electron clouds; *b*—σ-bonds (light shade) and delocalized π-electrons (dark shade)

atom interacts with the *p*-electrons of the adjacent carbon atoms. They are all arranged symmetrically around the ring and move along it. Thus, six π-electrons are not localized in pairs, like in the formation of ordinary double bonds, but constitute a general π-system, i.e., *circular conjugation* is effected:

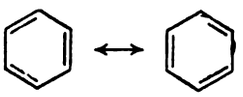


The distribution of the electron density in the benzene ring, determined by X-ray methods, indicates that the density is really distributed uniformly, i.e., the benzene nucleus has neither single nor double bonds, and all the bonds are the same. Figure 7.1*b* shows a model of the σ- and π-bonds of benzene. The dark shade represents the π-electron system, which forms the outer shell of a six-membered ring, and the light shade represents the sp^2-hybrid orbitals by means

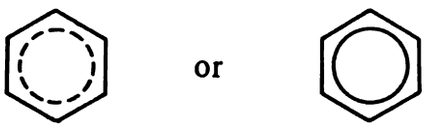
of which the σ-bonds are effected with the atoms of carbon and hydrogen.

A prerequisite of the complete delocalization of π-electrons, i.e., the completeness of conjugation, is the planar structure of the cyclic molecule and a definite number of π-electrons: in the benzene cycle, the number is six (*aromatic sextet*).

The true structure of a benzene ring is *mesomeric*, or intermediate between that represented by two extreme formulas:



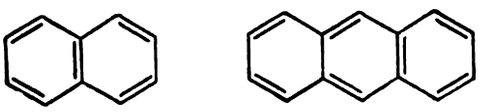
To denote benzene, use can be made of one of the formulas which indicate the intermediate nature of bonds:



However, Kekulé's formula is mainly used for representing the benzene molecule, all its disadvantages being taken into account.

There is a rule (Hückel, 1931), according to which aromatic stability is possessed by symmetric cyclic polyene systems whose number of π-electrons is $4n + 2$, where n is 0, 1, 2, 3, etc. Thus, aromaticity is possessed by systems having 2, 6, 10, 14, etc., π-electrons.

Examples of aromatic systems having 10 and 14 π-electrons are naphthalene and anthracene:

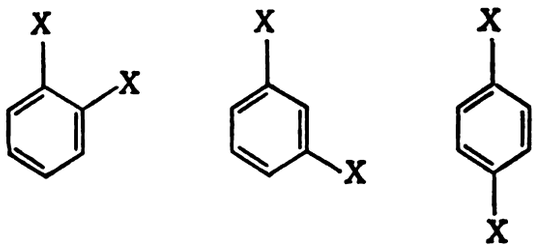


Naphthalene Anthracene

These compounds relate to the polynuclear aromatic hydrocarbons, which will be considered later (see Secs. 7.10 and 7.11).

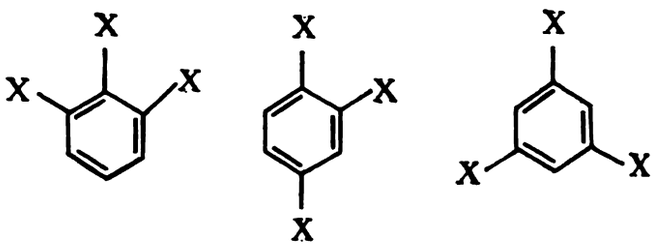
7.2. Isomerism of Benzene Derivatives. Nomenclature of Aromatic Hydrocarbons. Isomerism of benzene derivatives. Monosubstituted benzenes have no isomers, because all the carbon atoms in benzene are equivalent. Disubstituted benzenes exist as three isomers, which differ by the position of the substituents relative to one another. The position of the substituents is indicated by the prefixes *ortho-*, *meta-*,

para- or is denoted by numeral designations:



ortho-(1,2-) *meta-*(1,3-) *para-*(1,4-)

Three isomers have trisubstituted benzenes with the identical substituents

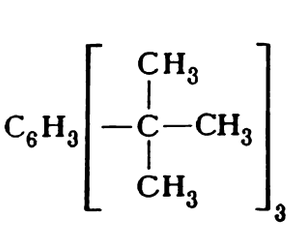


1,2,3- (Vicinal) 1,3,5-(Symmetrical)
1,2,4-(Asymmetrical)

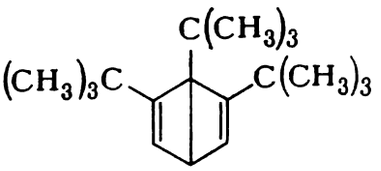
The number of tetrasubstituted benzenes with the same substituents is 3 too. Lastly, penta- and hexasubstituted benzenes with the same substituents have no isomers (for the same reason as monosubstituted compounds).

Valence isomers of benzene were obtained as a result of the investigations made in the 1960's. Such isomerism can occur when bonds in a molecule are redistributed, i.e., it can occur owing to the redistribution of electrons. Since the benzene molecule is stable, it can be isomerized under the action of a large amount of energy.

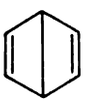
When tri-*tert*-butyl benzene I was exposed to ultraviolet light, a compound having structure II was obtained:



I



II



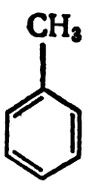
III

Later, bicyclic hydrocarbon III or *Dewar benzene*, C_6H_6, was isolated. The formula of Dewar benzene is similar to that of benzene proposed by Dewar in 1865, and hence its name.

Dewar benzene differs from benzene by the nature of bonds between carbon atoms, and also by chemical properties. Heated up to 90°C, it rapidly (while at room temperature, gradually) isomerizes to benzene.

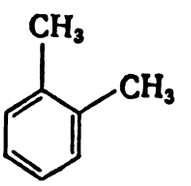
Benzene derivatives, which can be regarded as the products of substitution of the hydrogen atoms of benzene for alkyl radicals, are called *benzene homologues*. The general formula of such hydrocarbons is C_nH_{2n-6}. Unsaturated radicals (alkenyl and alkynyl) can also be hydrocarbon substituents. "Benzenoid" hydrocarbon molecules have two parts: the benzene nucleus and the side chain. The isomerism of these compounds is determined by the structure of radicals and by their dimensions and position.

Nomenclature. The names of hydrocarbons of the benzene series are composed from the names of the radicals of side chains with an addition of the ending **benzene.** Trivial names (given in parentheses) can be used for many of them:

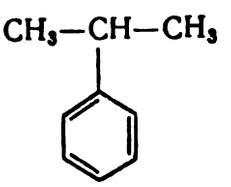


Methyl-benzene (toluene)

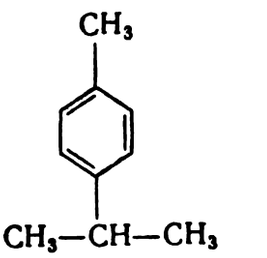
Ethyl-benzene



o-(or 1,2)-Dimethyl-benzene (*o*-xylene)



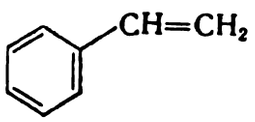
Isopropylbenzene (cumene)



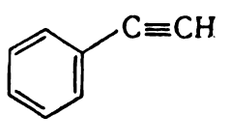
p-(or 1,4)-Methyl-isopropylbenzene (cymene)

Formulas can also be written in condensed form, e.g., 1,2-dimethylbenzene can be written as $1,2\text{-}C_6H_4(CH_3)_2$.

Examples of the names of benzene derivatives having unsaturated side chains are given below:

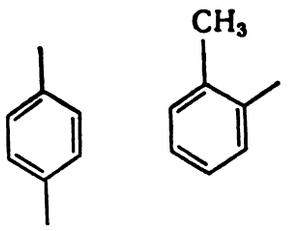


Vinylbenzene
(styrene)



Ethynylbenzene
(phenylacetylene)

The general name of aromatic hydrocarbons is *arenes*, while that of aromatic radicals, *aryls*. Examples of the names of radicals are: C_6H_5—, phenyl; $C_6H_4<$, phenylene (*o*-, *m*-, *p*-); $CH_3C_6H_4$—, tolyl (*o*-, *m*-, *p*-); $C_6H_5CH_2$—, benzyl; $C_6H_5CH<$, benzylidene. For instance,



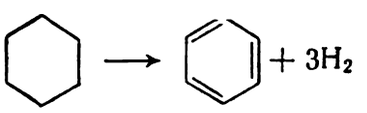
p-Phenylene *o*-Tolyl

The name *phenyl* is borrowed from *phene*, an old name for benzene.

7.3. Preparation of Benzene Homologues. Aromatic hydrocarbons can be synthesized on the basis of aromatic and nonaromatic compounds.

Arenes are obtained **from nonaromatic compounds** by several methods:

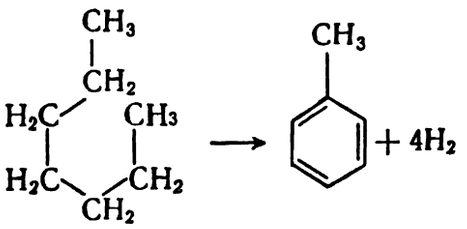
1. By catalytically dehydrogenating cyclohexane and its derivatives. This reaction was discovered by N. D. Zelinsky in 1911 (the catalyst is palladium black, at 300°C):



Platinum on alumina is now used industrially as a catalyst at a temperature of about 450°C. This reaction is the reverse of benzene hydrogenation (see Sec. 7.5).

2. By catalytically dehydrocyclizing alkanes, i.e., by eliminating hydrogen with the simultaneous closure of the ring (B. A. Kazansky, A. F. Plate, B. L. Moldavsky). As a catalyst, use can be made

of platinized coal at 300°C, and also of the oxides of chromium, molybdenum and vanadium. The most common use is made of chromium oxide on aluminium oxide at 500°C and 30 kg/cm²:



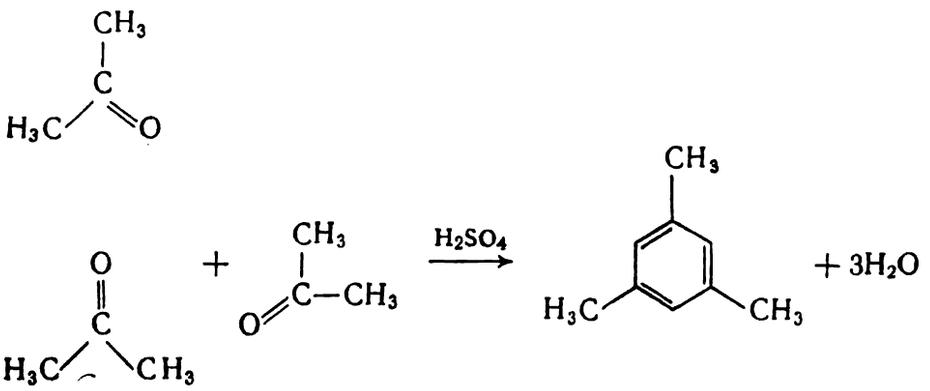
Heptane Toluene

Similarly, ethylbenzene and xylenes can be obtained from octane.

Both of the given reactions now constitute the basis of so-called *petroleum aromatization*; they make it possible to convert alkane and cycloalkane hydrocarbons of petroleum into aromatic ones, and this is of great practical importance.

3. By polymerizing acetylene and its homologues (see Sec. 5.4).

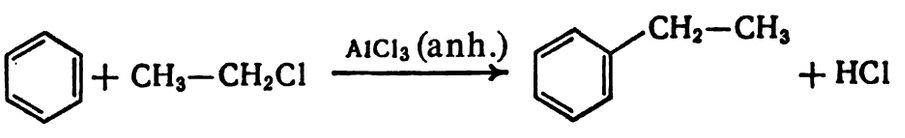
4. From acetone (condensation under the action of sulphuric acid):



The last two methods are used only in the laboratory.

Arenes are obtained **from aromatic compounds** by the following methods:

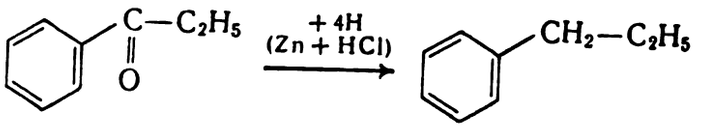
1. By alkylating aromatic hydrocarbons by alkyl halides and olefins (Friedel-Crafts reaction):



Ethylbenzene

This reaction is considered in greater detail in Sec. 7.5.

2. By reducing aromatic ketones:



Propylbenzene

Initial ketones are also obtained by the Friedel-Crafts reaction as an acid chloride acts on benzene (acylation reaction, p. 129).

3. By the Würtz-Fittig synthesis (1864). A mixture of an aryl halide and an alkyl halide is treated with metallic sodium:

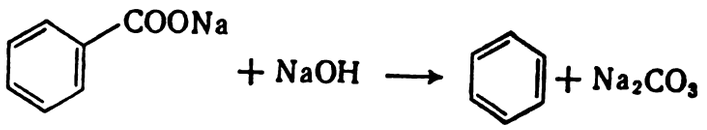
$$C_6H_5Br + BrC_2H_5 + 2Na \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5-C_2H_5} + 2NaBr$$

P. P. Shorygin (1881-1939) had ascertained that an organosodium compound, phenyl sodium, is at first formed, and then it reacts with ethyl bromide:

$$C_6H_5Br + 2Na \longrightarrow C_6H_5Na + NaBr$$

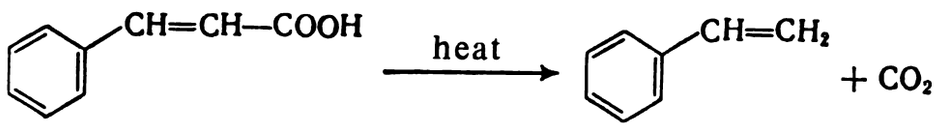
$$C_6H_5Na + BrC_2H_5 \longrightarrow C_6H_5-C_2H_5 + NaBr$$

4. From the alkali salts of aromatic acids by fusion with alkali or soda lime:



Sodium benzoate

5. By decarboxylizing unsaturated aromatic acids:



Cinnamic acid Styrene

7.4. Physical Properties. Benzene and its closest homologues are colourless liquids having a characteristic smell, and its higher homologues are solids (Table 7.1). The boiling and melting points depend on the dimensions and isomerism of side chains, and on the position of side chains in a cycle. Isomers with branched side chains usually have a lower boiling point than those with normal ones; *para*-isomers have the highest melting point. The density of arenes is always less than unity. They are all sparingly water-soluble, but they mix with organic solvents, such as alcohol, ether, acetone and liquid hydrocarbons, in all proportions. Liquid arenes are

good solvents of organic substances. They are highly inflammable and burn with a bright, very smoky flame. The vapours and liquids are toxic and some substances are carcinogenic, and therefore particular care must be taken when working with them.

TABLE 7.1. **Physical Properties of Some Arenes**

Name	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Benzene	+5.5	80.1	0.879
Toluene	—95	110.6	0.866
Ethylbenzene	—94	136.2	0.866
Xylene (dimethylbenzene)			
o-	—25	144.4	0.896
m-	—47	139.1	0.881
p-	+13	138.4	0.854
Propylbenzene	—99	159.2	0.861
Cumene (isopropylbenzene)	—96	152.4	0.862
Styrene (vinylbenzene)	—31	145.0	0.906
Phenylacetylene	—45	142.0	0.930

7.5. Chemical Properties of Benzene and Its Homologues. Electrophilic substitution in the aromatic series. Benzene has a saturated nature, while the C_6H_6 composition is clearly unsaturated (when there is a shortage of eight hydrogen atoms in comparison with hexane). This is expressed in the tendency towards substitution reactions and in stability to the action of oxidizing agents. Conversely, addition reactions occur with difficulty, and special conditions are needed for carrying them out.

Electrophilic substitution reactions are the most characteristic of aromatic compounds, although they are known to undergo also nucleophilic substitution reactions and radical reactions.

The mechanism of electrophilic substitution reactions in the aromatic series has some features in common with electrophilic addition to alkenes (see Sec. 4.5). It is also a two-stage ionic process. The aromatic nucleus, which possesses mobile π-electrons, is a convenient object for attack by electrophilic reagents.

The substitution process is preceded by the splitting of the reagent molecule XY with the formation of an electrophilic particle X^+ and an anion Y^-:

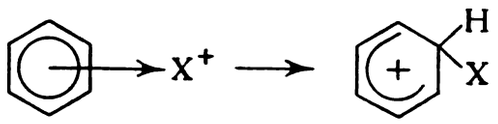
$$XY \rightleftarrows X^+ + Y^-$$

The electrophilic particle interacts with the π-electron cloud of the aromatic nucleus. It is attracted by the negative charge of the entire aromatic sextet of electrons; however, it is still not linked by

a true chemical bond, but forms the *π-complex*:

π-Complex

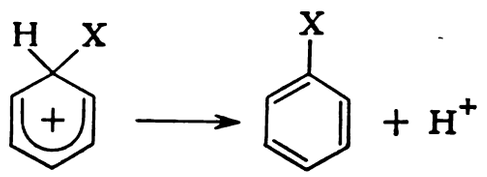
Then, two electrons from the six π-electrons of the ring are localized at one carbon atom and participate in the formation of a new covalent σ-bond with the entering substituent, while the remaining four electrons are distributed between five carbon atoms of the ring. As a result, an intermediate carbonium ion in which aromaticity is upset, the so-called *σ-complex*, is formed:



σ-Complex

In the formation of the carbonium ion, one of the six carbon atoms passes over from the state of sp^2 hybridization to that of sp^3 hybridization. Its configuration becomes *tetrahedral.*

The disturbance of the aromatic state is disadvantageous, because the aromatic nucleus possesses particular stability. Therefore, the proton is lost rapidly and aromaticity is restored:



The eliminated proton with the anion Y^- forms a by-product of the reaction:

$$H^+ + Y^- \longrightarrow HY$$

The electrophilic substitution reactions in the aromatic series are distinguished from those of electrophilic alkene addition mainly by rapid proton elimination. Aromaticity is restored more readily than the reaction occurs between the intermediate cation and the anion Y^- of a reagent. In the case of alkenes, the intermediate cation being formed produces, with the nucleophilic particle of the reagent (anion), a stable addition product.

Benzene undergoes mainly substitution reactions, because they do not require great energy. Only reagents rich in energy can be added, such as free chlorine atoms which originate photochemically

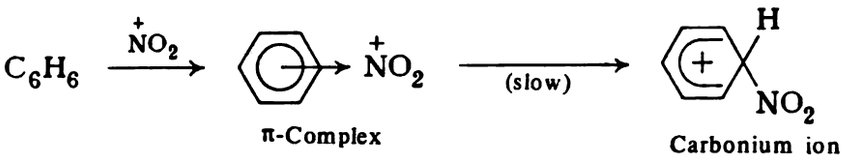
from chlorine molecules when exposed to light, hydrogen atoms which are activated by a catalyst, and energy-rich ozone.

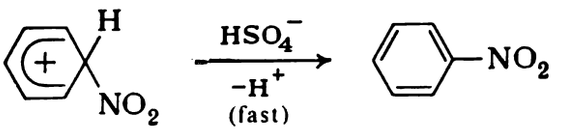
The electrophilic substitution reactions in the aromatic series are of great importance to syntheses used in the laboratory and in industry. The most important ones are given below:

1. Nitration, or the introduction of the nitro group NO_2. The reaction is usually carried out with a mixture of concentrated nitric and sulphuric acids. The attacking agent of nitration is the *nitronium ion* $^+NO_2$ formed in this mixture:

$$HNO_3 + 2H_2SO_4 \rightleftarrows \underset{\text{Nitronium ion}}{\overset{+}{N}O_2} + 2HSO_4^- + \underset{\text{Hydroxonium ion*}}{[H_3O]^+}$$

Later, the nitronium ion interacts with aromatic hydrocarbon, attacking the benzene π-cloud, as a result of which the π-complex is at first formed, and then the σ-complex (carbonium ion) with a covalent bond between the nitro group and the carbon atom of the benzene ring. At the last stage, the ion HSO_4^- expels the proton and a substitution product, the nitro compound, is formed:





Schematically, the reaction can be written as:

$$ArH + HONO_2 \longrightarrow ArNO_2 + H_2O$$

The presence of water in the reaction mixture hinders the reaction, because water participates reversely to the formation of the nitronium ion. Therefore, concentrated sulphuric acid is taken in excess to bind water which is formed in the reaction.

2. Halogenation of benzene nucleus is effected by halogens in the presence of catalysts. The most common use is made of the halides of aluminium and iron: $AlCl_3$, $AlBr_3$, $FeCl_3$, $FeBr_3$, etc.

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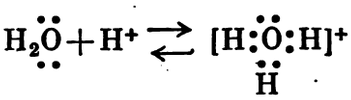
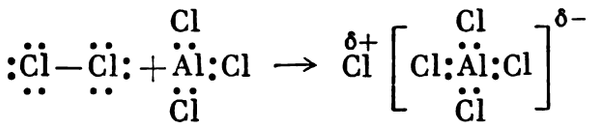
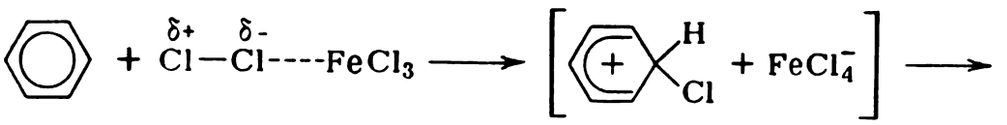
* The hydroxonium ion is present in the aqueous solutions of mineral acids. It is formed from the proton H^+ and the water molecule:



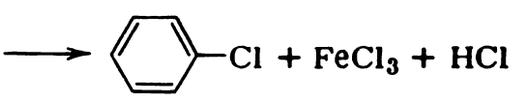
Catalysts promote the creation of an active electrophilic particle by polarizing the bond between halogen atoms. For example, in anhydrous aluminium chloride the aluminium atom has only six electrons on its outer orbital. It supplements this grouping to an octet at the expense of the free electron pair of the chlorine atom; as the electrons are extended, the second atom of the chlorine molecule becomes positively charged and, consequently, more electrophilic:



Anhydrous ferric chloride acts similarly:



σ-Complex with the participation of a catalyst



Chlorobenzene

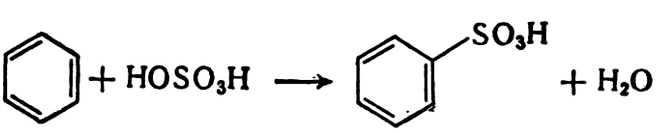
Halogen reactivity diminishes in the series:

$$F_2 > Cl_2 > Br_2 > I_2$$

Fluorine is too active, and therefore its derivatives are usually obtained indirectly. Direct iodination does not produce good results: iodine is poorly active, and therefore its derivatives are obtained also by means of a diazo compound (see Sec. 16.2).

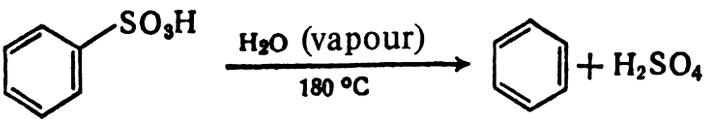
The action of chlorine and bromine on aromatic compounds under the conditions of a radical reaction (light, heat) causes the *replacement of hydrogen in the side chain* or *halogen addition* with the formation of cyclohexane derivatives (p. 129).

3. Sulphonation, or the substitution of the sulpho group for hydrogen in the benzene nucleus. The reaction is usually effected by heating aromatic hydrocarbon with concentrated sulphuric acid or oleum. As a result, aromatic sulphonic acids are formed:



Benzenesulphonic acid

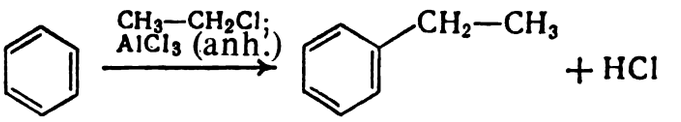
The sulphonation reaction, unlike the nitration and halogenation reactions, is reversible:



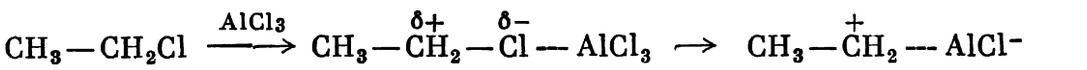
For greater details on the sulphonation reaction and its mechanism, see Sec. 13.3.

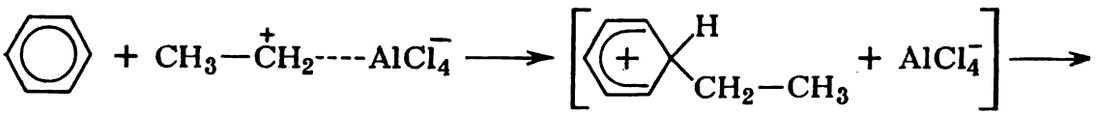
4. Alkylation, or the introduction of the alkyl group into the nucleus, which results in the formation of benzene homologues. Alkylation is effected in two ways:

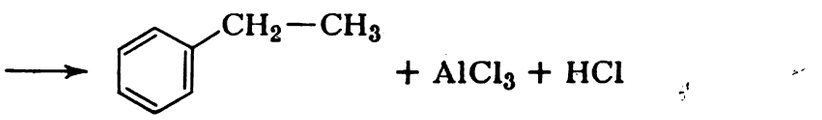
(a) By the action of alkyl halides on benzene in the presence of anhydrous aluminium halides as catalysts (Friedel-Crafts alkylation, 1877):



Like in halogenation considered above, the catalyst in the alkylation reaction also increases reagent polarity:



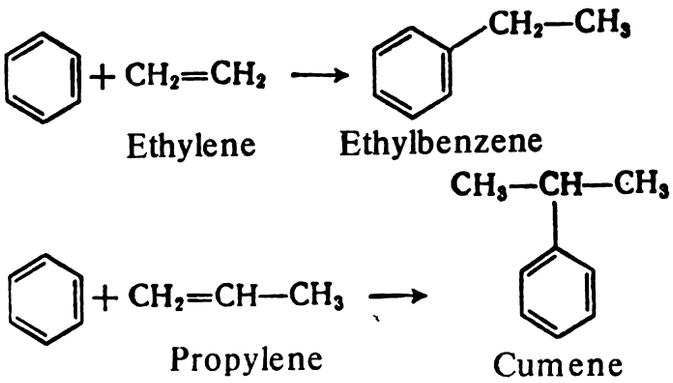




The reaction is complicated by further alkylation, because benzene homologues enter this reaction more readily than benzene. In this field, the investigations by the Russian scientist G. G. Gustavson are well known.

(b) Benzene alkylation by olefins in the presence of aluminium chloride or other catalysts (boron trifluoride, phosphoric acid). These reactions are widely used industrially for obtaining ethylbenzene and isopropylbenzene (cumene) from benzene and gases from

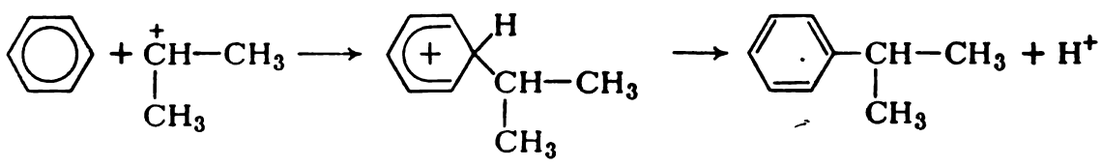
cracking of petroleum:



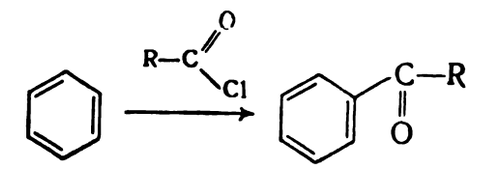
The reaction mechanism is similar to the preceding ones: the acid proton with the olefin molecule gives the carbonium ion

$$CH_3-CH=CH_2+H^+ \longrightarrow CH_3-\overset{+}{C}H-CH_3$$

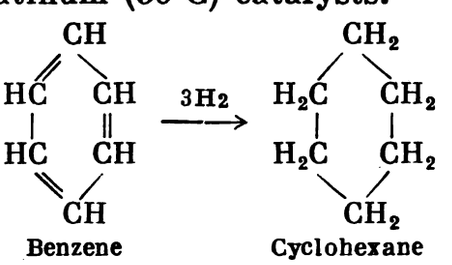
which reacts with benzene:



5. Acylation, or the introduction of the acyl group $R-\overset{|}{C}=O$ into the nucleus. Ketones are formed as a result of such reactions. This synthesis is known as Friedel-Crafts acylation. Acylating agents are acid chlorides or anhydrides in the presence of anhydrous aluminium chloride:

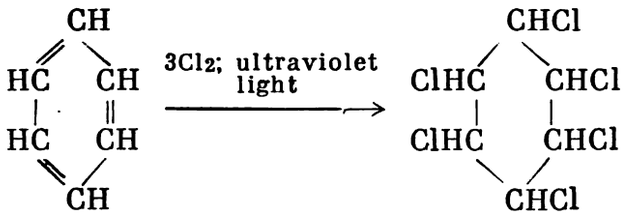


Addition reactions of aromatic hydrocarbons. 1. Hydrogen addition. Catalytic hydrogenation occurs smoothly in the presence of nickel (150°C) and platinum (50°C) catalysts:



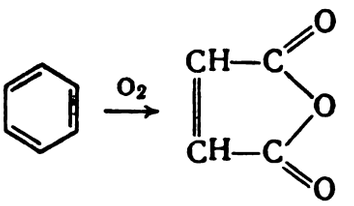
In this case, benzene derivatives produce cyclohexane derivatives. This is a practically important reaction, because cyclohexane is a good solvent, and it is also an intermediate for the synthesis of adipic acid and caprolactam.

2. Addition of chlorine in the presence of light (photochemical chlorination of benzene) gives hexachlorocyclohexane (hexachlorane), which is widely used as an insecticide:



Oxidation reactions. The stability of the benzene nucleus toward oxidation is one of the most important properties of aromatic compounds. Such oxidizing agents as nitric acid, the chromic-acid mixture, the potassium permanganate solution and hydrogen peroxide do not act on benzene under ordinary conditions. Benzene is even more stable than paraffin hydrocarbons toward these oxidizing agents. This is what also distinguishes aromatic compounds from compounds with double bonds.

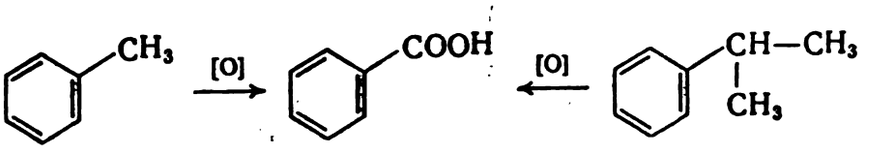
Maleic anhydride is obtained when atmospheric oxygen acts on benzene in the presence of the vanadium pentoxide as a catalyst at high temperature (400°C; this is an industrial process):



Maleic anhydride

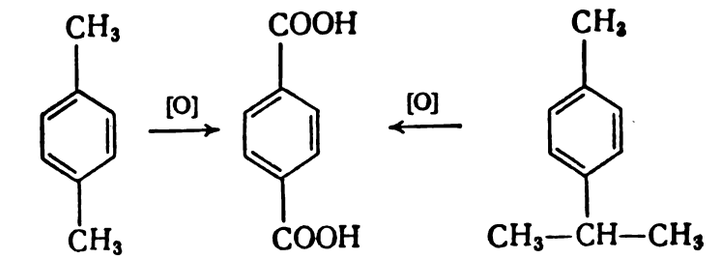
Side chains, or alkyl radicals, are oxidized when oxidizing agents act on benzene homologues. No matter how complex a chain is, it is destroyed under the action of strong oxidizing agents, except the carbon atom which is directly attached to the ring; it is converted to a carboxyl group.

Benzene homologues having one side chain give monobasic acid, i.e., *benzoic acid*:



Toluene Benzoic acid Cumene

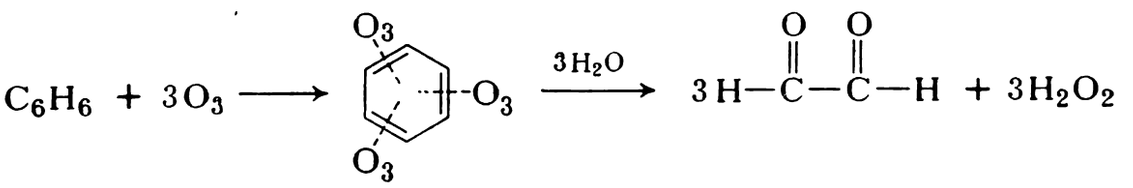
Homologues containing two side chains give dibasic acids:



p-Xylene Terephthalic acid *p*-Methyliso-propylbenzene

The position of side chains and their number can be determined by the aromatic acids formed as a result of oxidation.

Ozonization. Benzene molecule readily adds three ozone molecules, forming triozonide, which is an extremely unstable compound. Triozonide is destroyed under the action of water, and dialdehyde (glyoxal) is formed:



Benzene triozonide Glyoxal Hydrogen peroxide

7.6. Orientation in Electrophilic Substitution in the Benzene Nucleus. Many investigations are carried out to ascertain the regularities of substitution reactions in the benzene nucleus. Classical investigations in this field were made as early as the nineteenth century by the German scientist Holleman.

As we have already seen (Sec. 7.2), monosubstituted benzenes have no isomers owing to the equivalence of all the carbon atoms in benzene. When the second substituent enters the molecule, three isomers which differ by the mutual position of the substituents, the *ortho-*, *meta-* or *para*-isomers, can be formed.

The site of entry of a new electrophilic substituent is determined by the nature of the substituent already present in the aromatic nucleus. In other words, the substituent in the aromatic nucleus has a definite orienting effect in the course of further substitution; the substituent already present is said to direct the entry of the next substituent.

All the substituents can be divided into two groups by their orienting effect in the electrophilic substitution reactions in the benzene nucleus:

substituents of the first kind are oriented mainly in the *ortho-* and *para-*positions, they are *ortho-para-directing groups.* They include alkyl radicals, the groups —OH, —NH_2, —NHR, —NR_2, halogens, etc.;

substituents of the second kind are oriented mainly in the *meta-*position, and they are *meta-directing groups.* They include the groups —CF_3, —NO_2, —SO_3H, —COOH, —CN, etc.

Table 7.2 gives quantitative data obtained as a result of nitrating monosubstituted benzenes.

TABLE 7.2. **Orienting Effect of Various Groups in the Monobasic Benzene Nitration Reaction**

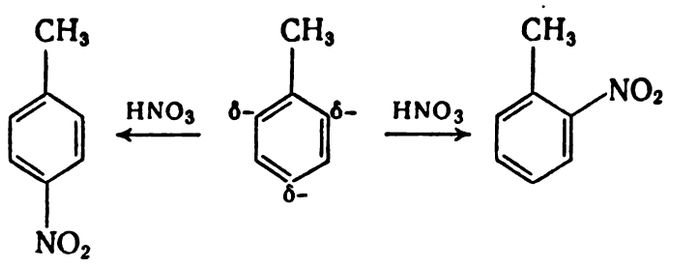
Substituent in the nucleus	Content of the isomer, %			Substituent in the nucleus	Content of the isomer, %		
	ortho-	*meta-*	*para-*		*ortho-*	*meta-*	*para-*
OH	40	—	60	CF_3	—	100	—
CH_3	56	4.0	40	NO_2	6.5	93.2	0.3
$C(CH_3)_3$	12	8	80	CN	17	81	2
F	12	—	88	COOH	18.5	80	1.5
Cl	30	1	69	$CHCl_2$	23	35	42
Br	36.5	1	62.5				

It follows from the examples that not all the substituents act selectively; for instance, the group $CHCl_2$ so acts that a mixture containing considerably large amounts of all the three isomers is formed. The ratio of the isomers being formed can also be affected by the nature of a reagent, its concentration, the type of a solvent, catalysts and temperature.

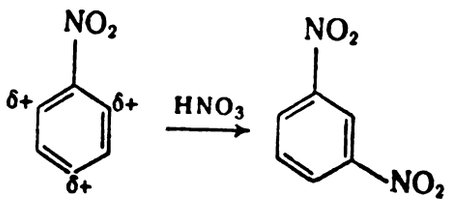
Substituents of the first and second kinds have a different effect on the reactivity of the benzene ring. *o,p*-Substituents (except halogens) activate the nucleus and facilitate the entry of a new substituent, as a result of which electrophilic substitution reactions occur considerably more readily than for benzene itself. *m*-Substituents hinder further electrophilic substitution.

Many theories have been proposed to explain the orienting effect of substituents. This effect has now been completely clarified by electron concepts. The *ortho-para-directors are electron-donating groups* which give electrons to the benzene ring. By increasing the electron density in the benzene ring, they make it more active in electrophilic substitution reactions (an exception are halogens, see Sec. 15.6). The *meta-directors are electron-accepting groups*, which draw out electrons from the ring. By reducing the electron density in the benzene ring, they decrease its activity in electrophilic substitution reactions.

Electron density changes mainly in the *ortho- and para*-positions with respect to the orienting substituent. Electron density in *ortho-* and *para*-positions *increases* under the action of *o,p*-substituents, and therefore the entering electrophilic group is mainly directed there. For example, when toluene is nitrated, a mixture of *ortho-* and *para*-isomers is mainly formed (see Table 7.2):



If the ring has the *m*-substituent, it withdraws electron density mainly from *ortho-* and *para*-positions, thus *reducing* their activity. The entering substituent is directed in the *meta*-position, from which the withdrawing of electron density is less, i.e., electron density in this case will be somewhat higher than that of *ortho-* and *para*-positions, and this determines the greater reactivity of this position. For example, the *meta*-isomer is mainly formed when the second nitro group is introduced into nitrobenzene (see Table 7.2):



To understand the nature of the orienting effect, it is necessary to have good knowledge of the properties of functional groups and the types of their mutual influence (*inductive and mesomeric effects*), and therefore this will be discussed in greater detail later.

7.7. Raw-material Sources of Aromatic Compounds. Practical Use of Benzene and Its Homologues. The main raw-material sources of aromatic compounds are pit coal and petroleum.

When pit coal is coked at 1000-1200°C, coke (75 per cent of the coal mass), coke gas (300 cubic metres per ton of coal), coal tar (2-5 per cent of the coal mass) and ammonia liquor are formed.

A large number of aromatic compounds is obtained from coal coking products. Coke gas contains about 25-35 g/m^3 of aromatic hydrocarbons. The coke gas is used as fuel after the hydrocarbons are separated by scrubbing in the cold with heavy oils. The gas con-

sists of methane, hydrogen, carbon monoxide, ethylene, acetylene, nitrogen, hydrocyanic acid, carbon dioxide, etc.

Coal tar is a blackish brown oil which is heavier than water and has a peculiar odour. Its composition depends on coal coking temperature. When the temperature is below 500°C, primary (low-temperature) tar containing many alkanes and cycloalkanes is formed. Tar obtained at high coking temperatures (1000°C and higher) contains mainly aromatic compounds (up to 300 various substances). Although the tar yield is only 2-5 per cent of the total coal mass, the overall amount of tar obtained is great, because hundreds of millions of tons of coal are coked.

Coal tar is subjected to distillation, and usually the following fractions, or cuts, are isolated:

1. *Light oil* (about 2 per cent of the total tar mass) is distilled up to 170°C; it contains benzene, toluene, xylenes, styrene, ethylbenzene, pyridine, etc.
2. *Middle oil* (up to 12 per cent of the total tar mass) is distilled in the 170-240°C range; it contains naphthalene, phenol and cresols.
3. *Heavy oil* (up to 10 per cent of the total tar mass) is distilled in the 240-270°C range; it contains naphthalene and its derivatives.
4. *Anthracene oil* (up to 25 per cent of the total tar mass) is distilled in the 270-360°C range; it contains anthracene, phenanthrene, etc.
5. *Pitch* (50-60 per cent of the total tar mass) is a solid tarry residue after distillation. It is used for making construction (roofing) materials, brick fuel, etc.

Individual compounds are isolated from fractions by redistillation and the crystallization of solid products. Substances having acidic properties (phenols) are isolated from mixtures by treatment with aqueous alkaline solutions, while those having basic properties (pyridine), by extraction with dilute sulphuric acid.

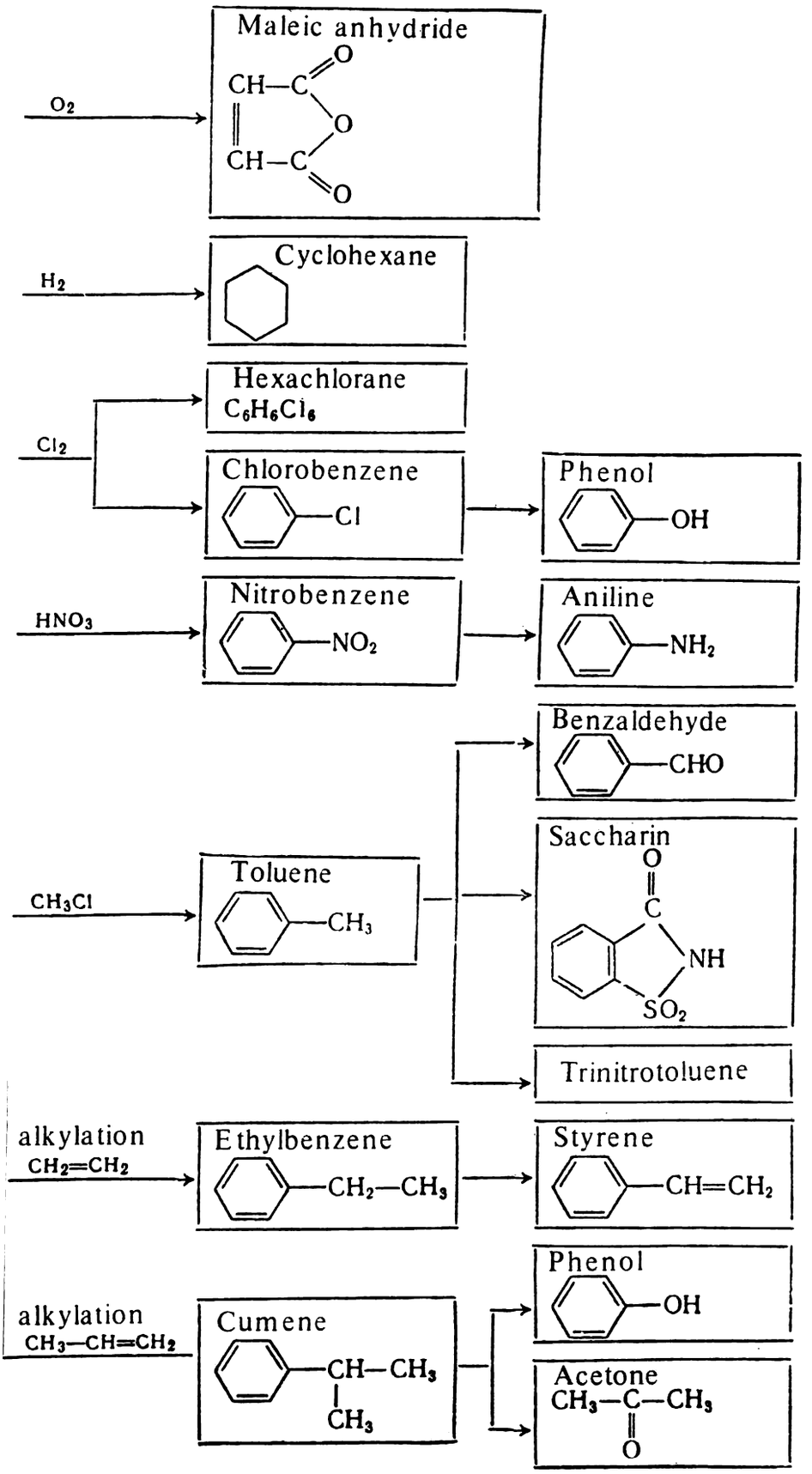
About 16 kg of benzene, 2.5 kg of toluene, 0.3 kg of xylenes, 40-60 kg of naphthalene, 5-20 kg of anthracene, and 20 kg of substances having a phenol nature are obtained from one ton of coal tar.

The coke-chemical industry is an important raw-material source for organic synthesis products. However, owing to the rapid development of the chemical industry, coke chemistry cannot meet the requirement for aromatic raw material. Moreover, it is difficult to obtain sufficiently pure products of coke-chemical origin.

A very important supplier of aromatic raw material is the *oil-refining industry.*

In some deposits, petroleum contains a considerably large amount of aromatic hydrocarbons, but aromatic compounds are, in the main, formed in the course of *catalytic aromatization* of the hydrocarbons contained in petroleum, i.e., in the catalytic dehydrocyclization of alkanes and the catalytic dehydrogenation of cycloalkanes (see

Industrial Use of Benzene



Sec. 7.3). In industry, this process is known as *catalytic reforming*. As a catalyst, use is made of platinum on alumina (500°C, 30-40 kg/cm^2). The raw material is the oil fraction which boils away below 180°C. In reforming products, the benzene-toluene-xylenes ratio is 1:4:5. Petroleum and its products of refining are considered in greater detail in Chap. 8.

Some examples of using benzene and its homologues are given in Diagram 7.1. The following compounds are important benzene derivatives:

o-Xylene is used for obtaining phthalic anhydride (see Sec. 12.16), which is a very important initial substance for producing polyesters and synthetic resins.

p-Xylene is used for obtaining terephthalic acid 1,4-$C_6H_4(COOH)_2$, which is an important raw material for the synthetic fibre Terylene (Dacron).

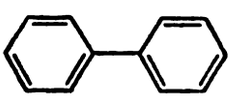
Durene (1,2,4,5-*tetramethylbenzene*) is obtained in catalytic reforming of petroleum and constitutes up to 10 per cent of the total mass of initial substances. It is used for synthesizing thermally stable polymers and solidifiers for epoxy resins.

Cymene (*p-methylisopropylbenzene*) is contained in many essential oils and in turpentine. It is used for obtaining terephthalic acid.

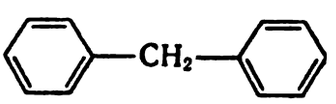
Styrene (*vinylbenzene*, *phenylethylene*) is a liquid with a pleasant odour. It was first isolated from the styrax resin. It is contained in the coal tar distillate, i.e., in light oil, and is produced industrially by dehydrogenating ethylbenzene. The chemical properties of styrene are determined by the presence of the benzene ring and the double bond in the side chain. A characteristic feature of styrene is its strong tendency to undergo polymerization (polystyrene formation).

POLYNUCLEAR AROMATIC HYDROCARBONS

Polynuclear aromatic compounds are substances which contain two or several benzene rings linked by the carbon-carbon bond. There are *compounds with isolated benzene rings*, in which the benzene rings are linked either directly or by the aliphatic chain, e.g.,



Diphenyl (biphenyl)



Diphenylmethane

and *compounds with condensed* (*or fused*) *benzene rings*. In condensed systems, benzene rings have common *ortho*-carbon atoms, such as in naphthalene and anthracene (see Secs. 7.10 and 7.11).

7.8. Polynuclear Aromatic Hydrocarbons with Isolated Benzene Rings. The simplest and most important representative of com-

pounds having isolated benzene rings is *diphenyl* (or *biphenyl*). It is a crystalline substance (m.p. 70°C, b.p. 254°C) which dissolves in alcohol, ether and other organic solvents. A small amount of biphenyl is contained in coal tar. It is prepared industrially by passing benzene vapours through molten lead:

$$2C_6H_6 \xrightarrow{600-700^\circ C} C_6H_5-C_6H_5+H_2$$

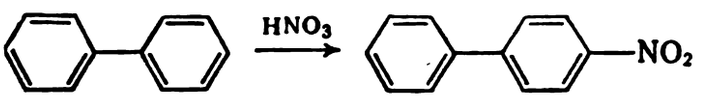
Biphenyl is obtained in the laboratory by the Würtz-Fittig reaction as metallic sodium acts on bromobenzene

$$C_6H_5Br+2Na+BrC_6H_5 \longrightarrow C_6H_5-C_6H_5+2NaBr$$

or when iodobenzene is heated in the presence of finely divided copper:

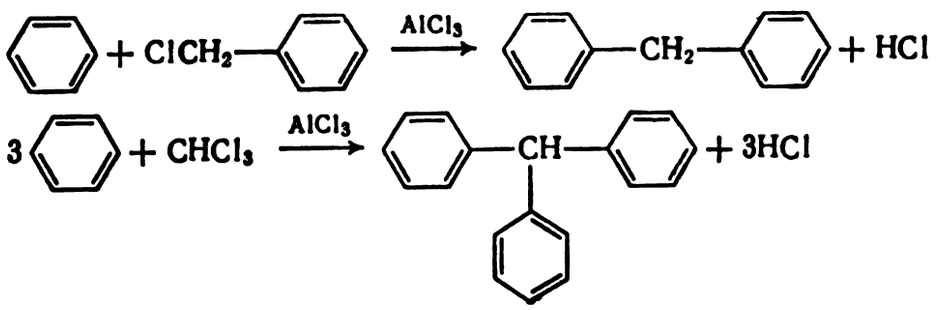
$$2C_6H_5I+2Cu \longrightarrow C_6H_5-C_6H_5+Cu_2I_2$$

Biphenyl is an aromatic hydrocarbon. In electrophilic substitution reactions, mainly *para*-isomers and small amounts of *ortho*-isomers are formed from it; thus, the phenyl radical exhibits properties of the *ortho-para*-directing group:



Biphenyl is thermally stable, and it is therefore used in the chemical industry as a heat carrier for heating various devices.

Diphenylmethane and *triphenylmethane* are crystalline substances whose melting points are 26°C and 92.5°C, respectively. It is most convenient to synthesize them by the Friedel-Crafts reaction:



Diphenylmethane has a pleasant odour of an orange, and it is therefore used in perfumery. It is also employed in various syntheses.

Triphenylmethane possesses considerably high reactivity owing to the especially great mobility of the hydrogen atom at the tertiary carbon atom:

$$(C_6H_5)_3C-Cl \xleftarrow{Cl_2} (C_6H_5)_3CH \xrightarrow{[O]} (C_6H_5)_3C-OH$$

Triphenylchloromethane — Triphenylcarbinol

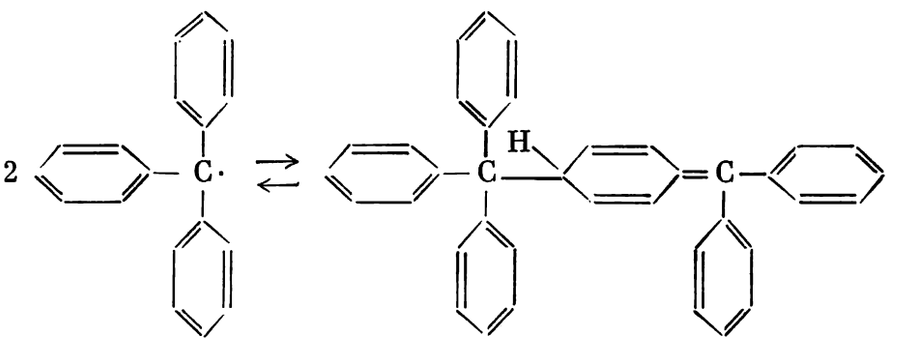
The amino and hydroxy derivatives of triphenylmethane are dyes.

7.9. Free Radicals. The effect of phenyl groups on the tertiary carbon atom in the triphenylmethane molecule is exhibited in the ability of this compound to form the free radical *triphenylmethyl.*

The discovery of triphenylmethyl is connected with Gomberg's investigations (1900) in the synthesis of the polyphenyl derivatives of ethane. For example, he expected to obtain hexaphenylethane under the action of metallic silver on triphenylbromomethane without oxygen:

$$(C_6H_5)_3CBr + 2Ag + BrC(C_6H_5)_3 \longrightarrow \underset{\text{Hexaphenylethane}}{(C_6H_5)_3C-C(C_6H_5)_3} + 2AgBr$$

But the compound obtained had some unexpected properties. Yellow colour appeared when its colourless solution was heated in benzene, and disappeared on cooling. It has been discovered that a *free triphenylmethyl radical* is actually formed, and it is in equilibrium with its dimer. At first, it was believed that the dimer is hexaphenyl ethane, but now it has been ascertained that the dimer has a more complex structure:



Triphenylmethyl Triphenylmethyl dimer

An elevation of temperature is conducive to the dissociation of the dimer, i.e., it helps to increase the content of triphenylmethyl, which is yellow. Triphenylmethyl reacts instantaneously with atmospheric oxygen, forming colourless triphenylmethyl peroxide $(C_6H_5)_3C-O-O-C(C_6H_5)_3$. The reaction with oxygen is used for detecting and quantitatively determining triaryl radicals.

Later, Paneth (1929) succeeded in obtaining short-lived radicals, i.e., methyl, ethyl, etc., in the thermal decomposition of lead alkyl compounds in the gaseous phase:

$$Pb(CH_3)_4 \longrightarrow Pb + 4H_3C\bullet$$

To this end, he passed a hydrogen stream, which entrained lead tetraalkyl vapours, through a quartz tube. The tube was greatly heated in a definite place, and the organolead compound decomposed there, as was evident from the deposit of metallic lead (lead mirror)

formed on the tube wall as a result of the foregoing reaction. Evidence of the presence of free radicals in the decomposition products was the disappearance of another mirror deposited earlier on the tube wall at a certain distance from the heating site. Free radicals, while reacting with the metal of the mirror, produced volatile compounds (R_2Hg, R_3Sb, R_2Zn, etc.), which were carried away with the hydrogen stream, and they were analyzed after being caught in a cooling trap.

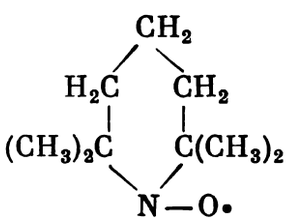
Short-lived free radicals (half-life of $H_3C\cdot$ is 0.005 s) can be formed as intermediate reaction products, and they can affect the course of a reaction owing to their high reactivity. Many practically very important reactions occur with the participation of free radicals, e.g., reactions of paraffin halogenation, thermal decomposition of hydrocarbons, oxidation, and polymerization.

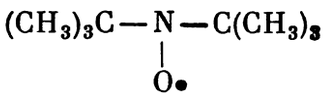
The free radical is a neutral particle having an odd number of electrons. Free radicals are unstable owing to the presence of an unpaired electron. The triphenylmethyl radical $(C_6H_5)_3C\cdot$ is rather stable, because the unpaired electron is not localized at the central carbon atom, and its density is distributed between the central carbon atom and all the carbon atoms of the three benzene rings (i.e., between 19 carbon atoms) owing to conjugation.

The free radical can become stable also when reagent molecules cannot easily enter the region where the unpaired electron is localized ("screening").

If both stabilizing factors, conjugation and screening, act simultaneously, free radicals can become very stable and act as ordinary organic substances in chemical reactions.

Soviet scientists (from the Institute of Chemical Physics of the USSR Academy of Sciences) succeeded in synthesizing "superstable" radicals, e.g., iminoxyl ones (Rozantsev's radicals), and isolating them in a crystalline state:



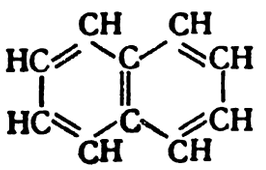


In iminoxyl radicals, the unpaired electron is "spread out" along the N—O bond, and this conserves energy; in addition, bulky neighbouring groups hinder access to the region in which the unpaired electron is localized. Iminoxyl radicals enter into ordinary chemical reactions, which occur also *without affecting* the unpaired electron. These radicals turned out to be strong inhibitors of oxidation and polymerization reactions. They are used in various ways owing to some of their interesting properties.

7.10. Polynuclear Aromatic Compounds with Condensed Benzene Rings. Naphthalene. The most important representatives of such compounds are naphthalene, anthracene and phenanthrene.

Naphthalene, $C_{10}H_8$, was discovered in coal tar in 1820. Its composition was established by A. A. Voskresensky (1858). It is a colourless crystalline substance (m.p. 80°C, b.p. 218°C) having a penetrating tarry smell, and readily sublimes. It evaporates even at room temperature, as is evident from its peculiar odour. Naphthalene is water-insoluble and readily dissolves in organic solvents. It is widely used as the moth balls in the household.

The carbon skeleton of the naphthalene molecule consists of two benzene nuclei which are condensed by two common neighbouring carbon atoms. The naphthalene molecule, like the benzene molecule, has neither double nor single bonds, although formulas I and II show five double bonds which alternate with single bonds. In this case, aromaticity is determined by the conjugation of 10 π-electrons (see Hückel's rule in Sec. 7.1).



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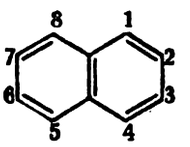


II

Naphthalene

In the naphthalene molecule, not all the carbon atoms are equivalent. There are α-carbons (positions 1, 4, 5, 8) and β-carbons (positions 2, 3, 6, 7).

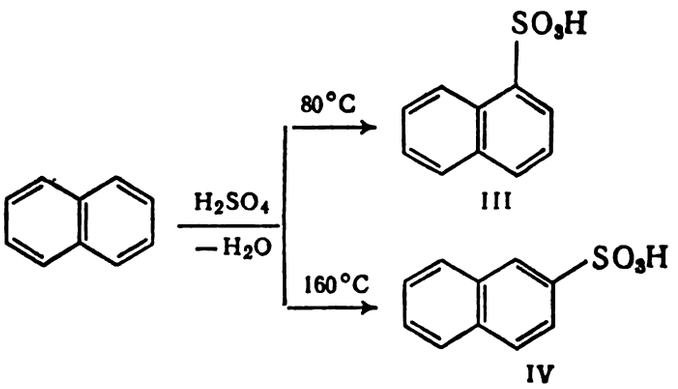
X-ray investigations of naphthalene crystals have shown that the naphthalene molecule has a plane structure, and the length of all the carbon-carbon bonds is intermediate between the lengths of single and double bonds.

Naphthalene derivatives have a greater number of isomers than benzene derivatives. Monosubstituted naphthalenes are known to have two isomers: α- and β-isomers. When the substituents are the same, disubstituted derivatives have 10 isomers (1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6-, 2,7-), and when the substituents are different, they have the number of isomers increased up to 14. The positions of the substituents in the naphthalene molecule are usually denoted by numerals. The position 1,8- is often called *peri* (from the Greek word meaning "near"), and the position 2,6-, *amphi* (from the Greek word meaning "on both sides").

Naphthalene by its *chemical properties* is an aromatic hydrocarbon and resembles benzene. But it exhibits a more unsaturated nature: it enters into addition reactions more readily than benzene. Substi-

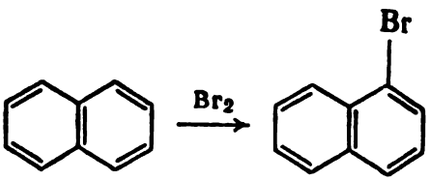
tution reactions occur more readily in α-positions than in β-positions. In some cases, the type of orientation can be changed by reaction conditions.

Substitution reactions. 1. Sulphonation is one of the substitution reactions characteristic of naphthalene; either α-naphthalenesulphonic acid III or β-naphthalenesulphonic acid IV can be obtained, depending on the reaction conditions:

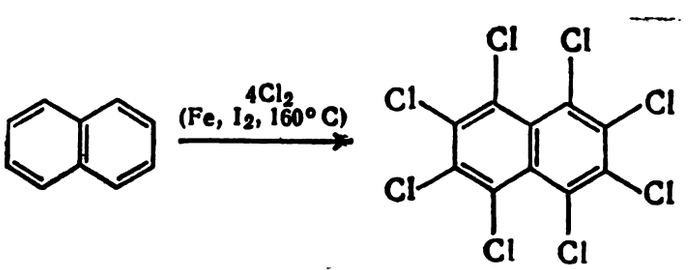


At low temperature, α-naphthalenesulphonic acid is formed. Since the α-positions of naphthalene are of higher reactivity, sulphonation in the α-positions occurs far more rapidly than in the β-positions. But β-naphthalenesulphonic acid is more stable than the α-isomer, and therefore α-naphthalenesulphonic acid is converted into the β-isomer when temperature rises.

2. α-Halogen derivatives are readily obtained when naphthalene is halogenated. For example, in bromination, α-bromonaphthalene is obtained:

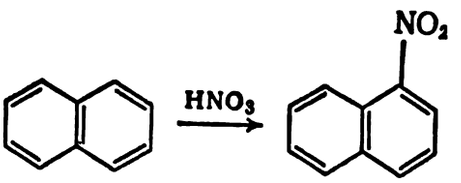


Among the chlorine derivatives of naphthalene, interest is now being taken in polychlorine derivatives up to the completely substituted perchloronaphthalene:

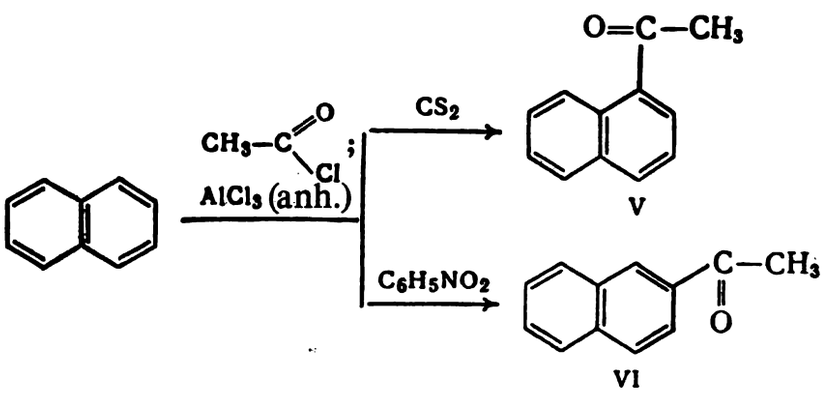


This wax-like substance, called *Halowax*, is used as a nonconductor.

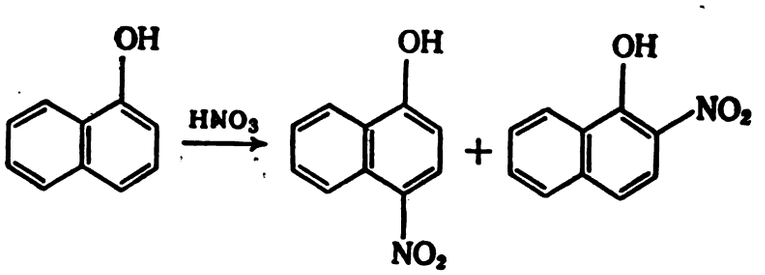
3. Nitration causes the formation of α-nitronaphthalene:



4. In acetylation, α-acetylnaphthalene V or β-acetylnaphthalene VI is obtained, depending on the conditions (temperature, solvent):

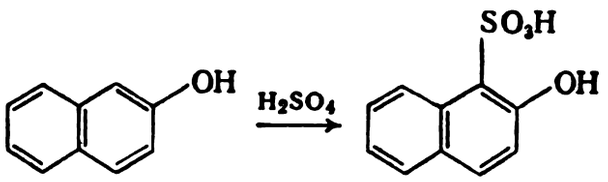


The rules of orientation in the naphthalene molecule are more complicated than those relating to benzene. If naphthalene molecule has an *o,p*-directing group (e.g., the OH group) in the α-position, the new substituent enters the same nucleus in position 4 or 2:



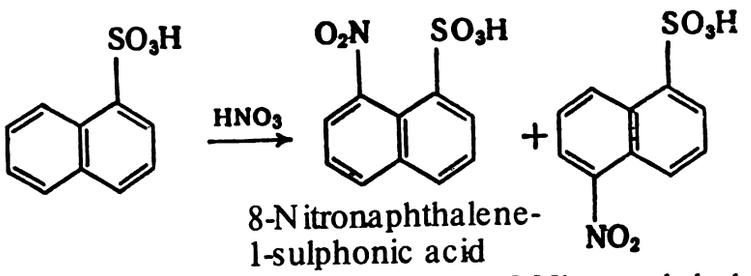
α-Naphthol (1-naphthol) | 1-Hydroxy-4-nitronaphthalene | 1-Hydroxy-2-nitronaphthalene

If such an *o,p*-substituent is in the β-position, the new substituent enters the nearest α-position:



β-Naphthol (2-naphthol) — 2-Hydroxynaphthalene-1-sulphonic acid

If the naphthalene molecule has a *m*-substituent (e.g., the SO_3H groups) in the α- or β-position, the new substituent enters another nucleus mainly in the α-position. For example, in the nitration of α-naphthalenesulphonic acid, we obtain:

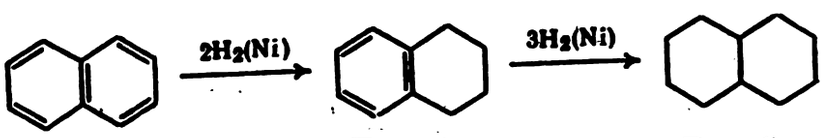


1 (or α)-Naphthalenesulphonic acid — 8-Nitronaphthalene-1-sulphonic acid — 5-Nitronaphthalene-1-sulphonic acid

In the nitration of β-naphthalenesulphonic acid, the nitro group also enters position 5 or 8.

Such an orientation becomes clear if we recall that the *o,p*-substituents *facilitate* further electrophilic substitution, while *m*-substituents *hinder* it. Therefore, in the latter case, the entry of the substituent into another nucleus is more advantageous.

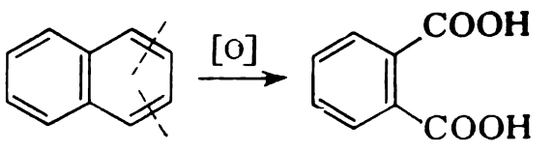
Addition reactions. An example is the naphthalene hydrogenation reaction. Naphthalene reacts with hydrogen more readily than benzene ring; at first, one nucleus is hydrogenated (160°C, 30 kg/cm²) and tetrahydronaphthalene, or *tetralin*, is formed; the end product of hydrogenation (200°C, 200 kg/cm²) is decahydronaphthalene, or *decalin*:



Naphthalene — Tetralin — Decalin

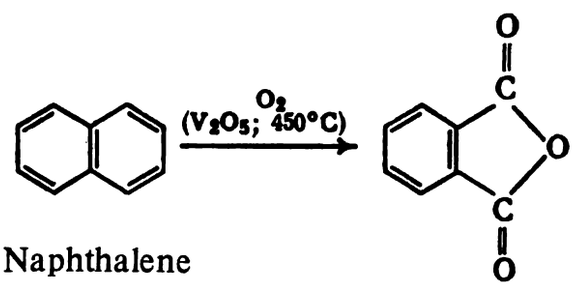
Tetralin and decalin, being liquids with high boiling points (207°C and 190°C, respectively), are solvents of resins and fats, and are additives to motor fuel.

Oxidation. Naphthalene is oxidized more readily than benzene; when it is being oxidized, one of the benzene rings is destroyed, while its α-carbon atoms turn into carboxyl groups, and dibasic phthalic acid is formed:



Naphthalene Phthalic acid

The reaction is carried out industrially by oxidizing naphthalene by atmospheric oxygen in the presence of vanadium pentoxide at 450°C. Phthalic anhydride is obtained practically, because phthalic acid loses water in the reaction:

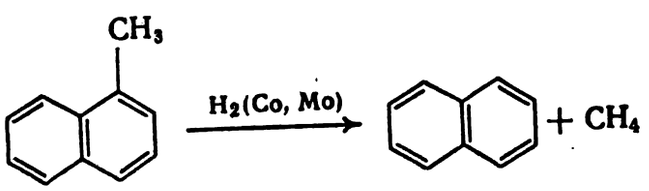


Naphthalene Phthalic anhydride

Phthalic anhydride is used very widely as an intermediate in various syntheses. Among the naphthalene oxidation products are also diketones, or *naphthoquinones* (see Sec. 11.9).

The main source of naphthalene is coal tar. Naphthalene is freed from acid impurities (phenols, etc.) by treatment with an alkaline solution; in this case, impurities pass into the solution, while naphthalene is squeezed out and then purified by sublimation.

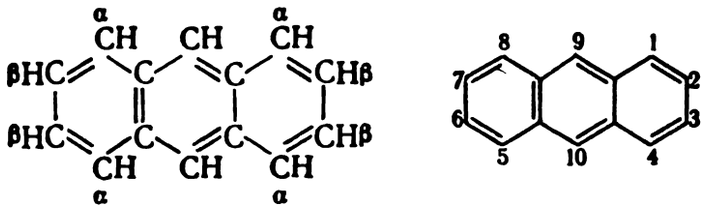
Another important source is crude oil. Catalytic petroleum reforming products contain a considerably large amount of methylnaphthalenes, which are converted into naphthalene by catalytic hydrodealkylation (750°C):



As we have already seen, naphthalene is used as raw material for obtaining phthalic anhydride, phthalic acid, naphthol sulphonic acids and other substitution products.

7.11. Anthracene, $C_{14}H_{10}$, is contained in a large amount in coal tar, in anthracene, or green, oil, from which it is isolated by crystallization and purified by sublimation. Pure anthracene is a colourless crystalline substance with slight blue fluorescence (m.p. 217°C, b.p. 354°C); it is insoluble in water and well soluble in boiling benzene.

Anthracene is a polynuclear aromatic hydrocarbon with three linearly condensed benzene rings of a planar structure:

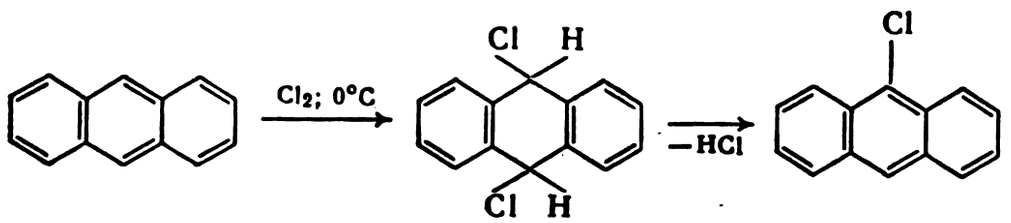


In the anthracene molecule, like in naphthalene, not all the carbon atoms hold the same position with respect to the common carbon atoms. There are the following positions: α- (1-, 4-, 5-, 8-), β- (2-, 3-, 6-, 7-) and *meso-* (9-, 10-). Thus, monosubstituted anthracenes can have three isomers: α-, β- and *meso*-isomers. Bonds are not completely equalized in the anthracene formula as well, and the shortest ones are α—β.

Anthracene is similar by its chemical properties to naphthalene and benzene, but it is more active. It exhibits an aromatic nature in *substitution reactions* (it is halogenated, nitrated and sulphonated), but it readily enters also into *addition reactions.* Positions 9 and 10 (*meso-*) are characterized by the greatest reactivity, and therefore substitution and addition reactions occur most readily in the central ring. As a result of addition in positions 9 and 10, both side rings acquire aromatic sextets and become stable.

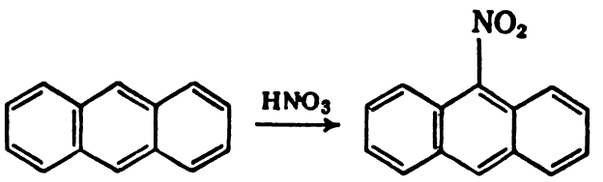
Among the **substitution reactions,** let us consider the following ones:

1. Halogenation. Chlorine or bromine at 0°C is at first added in positions 9 and 10, forming dichloride or dibromide, from which hydrogen halide is readily eliminated on slight heating and the substitution product is obtained:

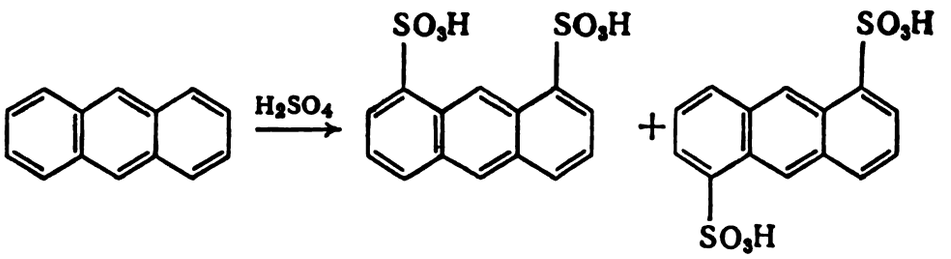


9-Chloroanthracene

2. Nitration. An unstable addition product is at first formed under the action of nitric acid, and then the substitution product, 9-nitroanthracene, is obtained after water is eliminated from it:



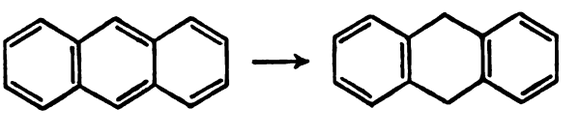
3. Sulphonation. Anthracene is readily sulphonated into the extreme ring, and then a mixture of α-disulphonic acids is formed:



1,8-Anthracene disulphonic acid

1,5-Anthracene disulphonic acid

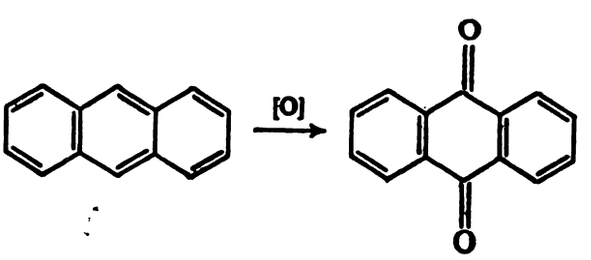
Among **addition reactions**, hydrogenation is of certain interest. Anthracene is readily hydrogenated in positions 9 and 10 by nascent hydrogen, e.g., by sodium in boiling alcohol:



9,10-Dihydroanthracene

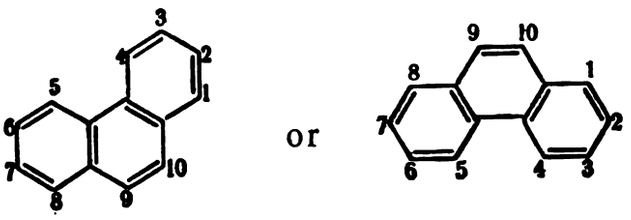
In exhaustive catalytic hydrogenation, perhydroanthracene, $C_{14}H_{24}$, is formed.

The **oxidation** of anthracene by the chromic-acid mixture and other oxidizing agents results in the formation of anthraquinone (see Sec. 11.9):



Anthracene is an industrial product from which dyes, e.g., alizarin, are obtained. A large amount of anthracene is used for producing anthraquinone.

7.12. Phenanthrene. The hydrocarbon phenanthrene, $C_{14}H_{10}$, is an angular isomer of linear anthracene:



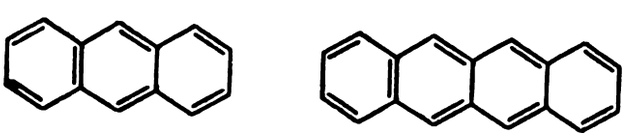
This colourless crystalline substance (m.p. 100°C, b.p. 340°C) is contained in the anthracene fraction of coal tar.

Phenanthrene is of an aromatic nature. It resembles naphthalene by its chemical properties, but differs from it by greater unsaturation. As a result, addition reactions occur readily. Positions 9 and 10 are characterized by especially great activity. This bond in the phenanthrene molecule is similar to an ordinary double bond.

Phenanthrene itself is of no practical interest, but many complex natural compounds which are of physiological significance contain the phenanthrene ring. They are steroids, sex hormones, vitamin D, alkaloids and other substances, which will be considered later.

7.13. Higher Condensed Aromatic Hydrocarbons. Higher fractions of coal tar contain a considerably large amount of complex condensed-ring compounds. They can serve as starting material for synthesizing various intermediates, dyes and medicinals. By their structure (by the position of rings), some polycyclic aromatic compounds are similar to anthracene, while others, to phenanthrene.

In the anthracene molecule, the benzene rings are condensed *linearly* (the ring centres are on one straight line). Anthracene can be called 2,3-benznaphthalene. The following hydrocarbon having four linearly condensed rings bears the name of 2,3-benzanthracene, and its trivial name is *naphthacene* or *tetracene* (m.p. 343°C).



Anthracene Naphthacene

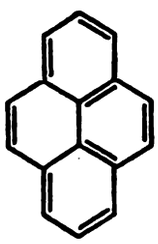
The general name of such compounds is *acenes*; they are *linearly* built systems, and are coloured.

Aromatic properties decrease (one electron sextet is spread out) as the number of rings increases. These compounds are similar to

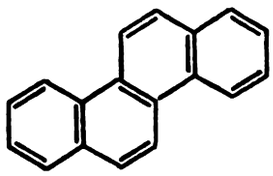
polyenic hydrocarbons with conjugated bonds (they are readily oxidized).

The partially hydrogenated derivatives of tetracene are the basis of important antibiotics of the tetracycline series.

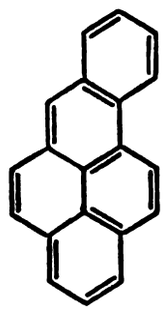
Polynuclear systems whose structure is similar to that of phenanthrene, where the centres of not all the benzene rings are on one straight line, are called *angular systems.* Their aromatic nature is more pronounced than that of acenes (they have two electron sextets). Examples are pyrene, chrysene and benzpyrene:



Pyrene



Chrysene



Benzpyrene

It has been ascertained that some polynuclear cyclic compounds cause eczema and malignant tumours, i.e., they possess carcinogenic properties. An example is benzpyrene, $C_{20}H_{12}$, which is one of the most dangerous carcinogens. It is formed in the pyrolysis of hydrocarbon fuels when there is a shortage of oxidizing agents. Coal coking products and the exhaust fumes of motor vehicles contain many substances which have carcinogenic properties.

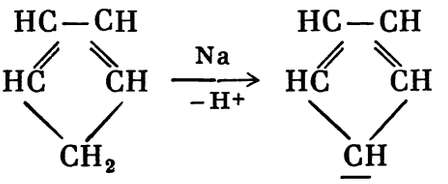
7.14. Nonbenzenoid Aromatic Compounds. There are compounds in whose molecules the π-electrons are in cyclic conjugation, although the molecules have no benzene rings. In this case, the aromatic nature is most pronounced in compounds whose ring has six π-electrons, i.e., in compounds where the aromatic electron sextet is formed.

Such compounds are known as *nonbenzenoid aromatic compounds.* The aromatic nature can be possessed not only by carbocyclic compounds, whose skeleton consists of carbons alone, but also by heterocyclic compounds, which have other atoms, such as oxygen, nitrogen and sulphur, in the ring.

Besides neutral molecules, some organic ions (anions and cations) can exhibit aromatic properties. Characteristic examples are the *cyclopentadienylium anion* and the *tropylium cation.*

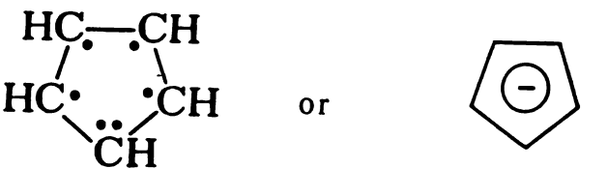
1,3-*Cyclopentadiene* and the *cyclopentadienylium anion.* The hydrocarbon C_5H_6 is a cyclic diene hydrocarbon having an unsaturated nature. Unlike other similar compounds, it possesses acidic properties which are even stronger than those of 1-alkynes. Hydrogen of the CH_2 group is capable of being replaced by metal. Under the

action of alkali metals in organic solvents, a proton is eliminated and a compound bearing a negative charge $(C_5H_5)^-$, the cyclopentadienylium anion, is formed:

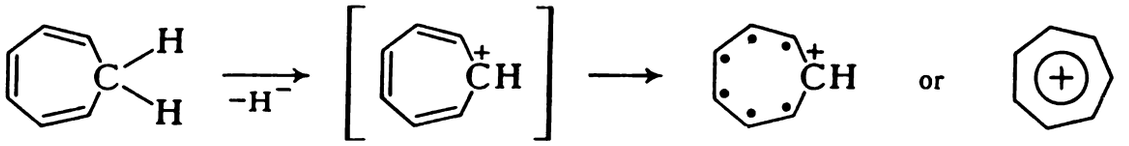


1,3-Cyclopentadiene ion — Cyclopentadienylium ion

In this anion, two unshared electrons are not localized at one carbon atom, but form an aromatic π-electron sextet with four π-electrons of two double bonds. In the anion, all the carbon atoms are equivalent:



Tropylium cation. As a result of the abstraction of the hydride ion H^- from the cycloheptatriene molecule, six π-electrons remain in the ring; they are delocalized, forming a stable electron sextet:



Tropylium ion

The tropylium cation $(C_7H_7)^+$ is very reactive.

Azulene, $C_{10}H_8$, is a representative of bicyclic compounds which do not contain benzene rings, but have an aromatic nature. It is a dark-blue crystalline substance. Azulene is isomeric toward naphthalene, but, unlike the latter, rings of different sizes, five- and seven-membered rings (formula I) are condensed in its molecule:

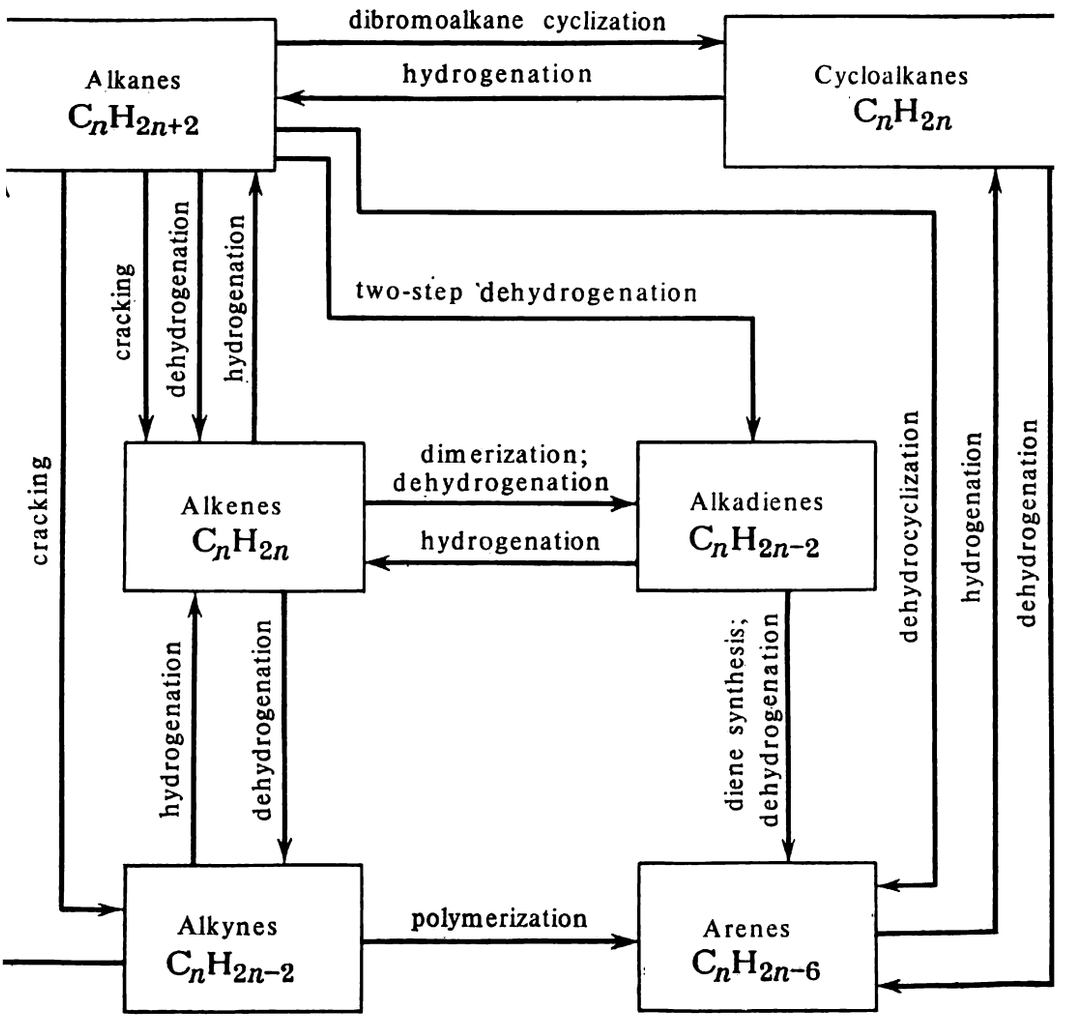
I II

Azulene is less stable than naphthalene; it is isomerized into naphthalene when heated above 350°C without air. The azulene molecule is polar ($\mu = 1.0$D). Five- and seven-membered rings

ıtain six delocalized electrons each, and therefore the azulen lecule (formula II) is a combination of two ions: the cyclopenta nylium anion and the tropylium cation. But it has been asce ned that there is no complete ionization, and 10 π-electron 'ticipate in the formation of a common π-electron cloud.

'.15. Hydrocarbons as the Basis of Organic Chemistry. Variou ıes of hydrocarbons were described in the previous chapters. Ne sses of organic compounds can be formed by replacing hydroge ms in hydrocarbons with other atoms or groups. In the last de les, hydrocarbons became the main type of raw material for th anic synthesis industry. Numerous intermediate products obtaine ustrially from hydrocarbons are used further for synthesizing rul , plastics, synthetic fibres, detergents, dyes and pharmaceuticals ndustrial methods of interconverting hydrocarbons of differen nologous series are now widely used. Diagram 7.2 gives an ide these conversions.

ıGRAM 7.2. **Hydrocarbon Interconversion**



Chapter 8

PETROLEUM

8.1. Petroleum, Its Refining and Application. Petroleum is one of the most important natural minerals and one of the principal sources of technical fuel. At present, the main types of fuel are used in approximately the following proportion: pit coal, 32 per cent; petroleum and gas, 59 per cent; water power, 7 per cent, and atomic energy, 2 percent. The principal deposits of petroleum and gas in the Soviet Union are in North-West Siberia.

Various hypotheses were proposed for the *origin of petroleum.* Advocates of the organic origin of petroleum hold that it was formed from the products of decomposition of marine organic substances. To prove this, they maintain that petroleum contains substances characteristic of living organisms: fatty acids, steroids, hormones and chlorophyll. Advocates of its inorganic origin suppose that hydrocarbons could have been formed from elements at the initial stage of the formation of planets. One of the arguments in their favour is the detection of considerably great amounts of methane in the atmospheres of large planets. Hydrocarbons, amino acids and other compounds found in living organisms and in their decay products were detected in celestial bodies by gas chromatography and spectroscopy.

According to the advocates of the carbide theory (which was first stated by Mendeleyev), petroleum was formed under the action of water on the carbides of metals located in the depths of the Earth. This hypothesis explains why rich petroleum deposits are found at a depth of 2-3 kilometres. At such a depth, petroleum could not originate from living organisms.

Petroleum has been known to Man from hoary antiquity (from several centuries B.C.).

Gummy bitumen formed from petroleum which had risen to the surface was used as binding construction material and as a medicinal (it was used to heal scabies, abscesses, and pain in the ears and joints). Ancient Greeks, Romans and Chinese used petroleum for military purposes. The Arabs had petroleum distillation devices in the first century B.C.

Until the middle of the nineteenth century, petroleum was extracted primitively, i.e., manually from shallow wells. The first borehole

began to operate in Russia (in Ukhta) in 1855. In the early 1860's, a switch-over was made from the manual technique of drilling to a mechanical, percussion one, and petroleum began to be distilled.

At the initial stage of development of the petroleum industry, the main product was kerosene, which was used for lighting. Gasoline was thrown away (it was poured into ravines and the sea) because of the danger in handling it. After kerosene distillation, petroleum which remained was burned in furnaces. In the 1880's, it was ascertained that aromatic hydrocarbons could be obtained from petroleum. The world's first experimental cracking apparatus was proposed by the engineer and designer V. G. Shukhov (1890).

Crude oil is an unctuous liquid whose colour ranges from light brown to black (depending on the deposit). Different types of petroleum differ in not only colour, but also odour and viscosity. Petroleum density is in the 0.7-0.9 range.

By its *composition*, petroleum is a composite mixture whose main part consists of paraffin, cycloparaffin (naphthene) and aromatic hydrocarbons. Lower paraffin gases accompany petroleum (accompanying oil gas); they are partially dissolved in it, and when there is a great amount of them, petroleum fountains from the earth under their pressure. Higher solid hydrocarbons are also dissolved in liquid hydrocarbons.

Petroleum which contains a large amount of paraffin hydrocarbons is called *paraffinic oil.* This petroleum is found near Grozny (USSR), in the Central Asia and in Pennsylvania (USA). Petroleum which is rich in cycloparaffins is known as *naphthenic oil*, such as that extracted in Baku. Some deposits, such as those in the Urals, the Ukraine, Romania and Borneo, contain substantial amounts of aromatics.

Besides hydrocarbons, petroleum contains small amounts of compounds having oxygen (naphthenic acids, phenol), sulphur (thiophene and its derivatives) and nitrogen (various heterocyclic compounds).

Petroleum is a very valuable fuel; like gas, it has a high calorific value. When one kilogram of petroleum burns up, 46,000 kJ are evolved. Petroleum excels other types of fuel (except gas) by its calorific value. It is easy to convey and store.

Oil distillation. Petroleum refining usually ends with its distillation, i.e., with its division into cuts, or fractions, which have different boiling points. This is a *physical method* of petroleum refining.

The most important fractions are the following:

1. The fraction up to 40°C consists of gaseous products dissolved in petroleum, being normal and branched alkanes C_1-C_5. Liquefied oil gas consists of mainly propane and butane. Low-boiling gasoline gas is obtained when oil gas is cooled under pressure and passed through columns filled up with coke and sprinkled with heavy oil.

2. The *gasoline fraction* (40-180°C) contains the hydrocarbons C_5-C_{10}, i.e., normal and branched alkanes, cycloalkanes, alkyl benzenes, over 100 various compounds in all.

3. The *kerosene fraction* (180-270°C) contains the hydrocarbons C_{10}-C_{15}; it is used in cracking and as fuel for jet engines.

4. *Gas oil* (solar oil, 270-360°C) contains the hydrocarbons C_{12}-C_{20}; it is used for obtaining lubricants, as diesel fuel, and in cracking.

5. Oil residues which boil above 360°C are usually called *mazut* (40-50 per cent of the original petroleum); they are used in cracking and for obtaining heavy lubricants, petrolatum, paraffin, etc.

The heavy residue which remains after all the fractions are distilled, known as *goudron*, and which contains higher paraffins up to C_{50}, is aerated and used as *asphalt* for building roads. Coke also can be obtained from goudron. Petroleum with a high goudron yield is known as *asphaltum oil.*

Light fractions can be divided by redistillation into parts whose boiling points are in a narrower range. For example, the following are isolated from the gasoline fraction: petroleum ether (40-70°C), aviation gasoline (70-100°C), motor gasoline (100-120°C), etc. Narrower kerosene fractions can also be thus obtained. Individual hydrocarbons, such as pentanes, hexanes, cyclopentane, cyclohexane, their methyl derivatives and aromatic hydrocarbons (benzene, toluene, xylenes) are isolated from high-boiling gasoline fractions.

About 150 pure hydrocarbons with boiling points up to 250°C have been isolated from petroleum and identified. Distillates are purified to remove sulphides and other impurities.

Modern transport requires an ever greater amount of fuel, especially high-quality fuel. The main type of fuel for carburetor internal-combustion engines is gasoline, which accounts for only 15 per cent of the total amount of crude oil when the latter is distilled. In addition, the quality of gasoline obtained by direct distillation does not meet the requirements of modern technology. Petroleum is refined chemically in order to increase the yield of gasoline and improve its quality.

Chemical petroleum refining. The classical works by V. V. Markovnikov and his pupils (M. I. Konovalov, N. M. Kishner, etc.) initiated a detailed study of the chemistry of petroleum. Modern technological means of oil refining, i.e., catalytic cracking and reforming, are associated with the outstanding works by N. D. Zelinsky and his pupils.

Cracking is a process in which molecules of high-boiling hydrocarbons are split up into more simple, low-boiling ones, making it possible to increase the yield of gasoline from petroleum by several times (up to 60-80 per cent).

Chemical methods of petroleum refining are a complex chain of chemical processes: splitting, isomerization, dehydrogenation and

dehydrocyclization (aromatization). In petroleum refining, use is also made of alkylation, dimerization, etc. All these processes engender many gaseous products (paraffins and olefins), and also aromatic compounds, which are used as raw material for the basic organic synthesis industry. A special industry, the *petrochemical industry*, is engaged in primary chemical petroleum refining. The appropriate acids are obtained by directly oxidizing the isolated lower paraffins (propane, butane), and valuable intermediates, by chlorinating paraffins. Butane and butylenes are raw material for obtaining divinyl, which is a monomer for producing synthetic rubber. Lower olefins and aromatic hydrocarbons are very important intermediates of organic synthesis. It is impossible to synthesize high-molecular-weight compounds without readily available and inexpensive petrochemical raw material: monomers.

Many microorganisms can exist on media where petroleum hydrocarbons are the only source of carbon. For them, the most preferential ones are normal paraffins, beginning with dodecane (C_{12}). In industry, a microbiological method of obtaining a protein-vitamin concentrate from petroleum hydrocarbons is now used.

Petrochemical raw material is used to produce biologically active substances, medicinals, aromatic substances, dyes, solvents, plasticizers, lacquers, mastics, enamels, facing material, initiators of polymerization and inhibitors of corrosion.

Petroleum is becoming more and more important to the national economy and defence. Petroleum products are used as fuel by transport (planes, automobiles, diesel locomotives and diesel ships) and farm machinery (tractors, harvesters and tow tractors). Petroleum oil is used for electric substation transformers, engines, various machine-tools, etc.

Growing concern is now expressed to the effect that petroleum reserves in the world are not very large, and that petroleum consumption for energy purposes should be reduced. Mendeleyev spoke about this even in his day, saying: "There in no sense in using petroleum as fuel; it is like dumping money into the fire."

At present, it is very important to make a comprehensive approach to petroleum refining: there should be a maximum yield of the most valuable product with minimum wastes, and the unused raw material and reagents should be repeatedly returned into the refining system (circulation processes).

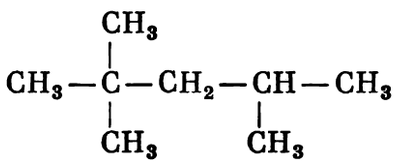
In the last two decades, petroleum has been one of the main sources of chemical raw material; one ton of petroleum gives just as much raw material for the chemical industry as 15 tons of brown coal.

The petrochemical industry is the basis for the development of the organic synthesis industry, both at present and in the future.

Detonation of fuel and the octane number. The efficiency of an engine depends on the degree of compression of the fuel mixture.

The degree of compression is the ratio of the initial volume of the gasoline-air mixture, which is sucked into the cylinder, to the final volume after compression. Fuel can be saved and engine power enhanced by increasing the compression ratio. But a growth in the power of an engine, such as that of an automobile, means greater speed and lifting power and less fuel consumption. When fuel burns up normally, the pressure inside the cylinder continuously rises and the combustion rate is 20-25 m/s. When it burns up abnormally, *detonation* occurs, i.e., the gasoline-air mixture bursts into flame instantaneously with an explosion, the combustion rate being 1500-2000 m/s. In this case, an enormous amount of gases is liberated, causing a sharp rise in pressure inside the cylinder. The impact of the detonation wave against both the cylinder wall and the piston produces motor "knocking". As a result of the detonation, the motor works improperly, engine power diminishes, a greater amount of fuel is consumed, and individual parts of the motor burn out and break.

Isooctane (2,2,4-trimethylpentane) was selected as an example of fuel having good antidetonation properties. Its formula is:



Its octane number is taken as 100. *n*-Heptane was taken as an example of fuel having poor antidetonation properties. Its formula is

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

and its octane number is taken as zero.

The test gasoline is compared with the reference mixtures of *n*-heptane and isooctane. For example, gasoline having an octane number of 80 possesses the same antidetonation properties as a mixture of isooctane and *n*-heptane in the 4:1 ratio. The higher the octane number, the better is the quality of the fuel. An investigation of many hydrocarbons has shown that, in the paraffin series, the octane number decreases as the normal chain of carbon atoms grows longer, and increases as the chain becomes branched. Olefins have a higher octane number, which increases as the double bond is displaced towards the centre of the molecule. The octane numbers of cycloparaffins are even higher, while aromatic hydrocarbons are the most stable toward detonation.

In World War II, the demand for high-octane fuel was enormous and the production of individual isoparaffin hydrocarbons became the leading branch of the petrochemical industry. The world production of synthetic paraffins amounted to millions of tons. Two techniques were mastered: the dimerization of olefins with the subsequent

catalytic hydrogenation of the product and the alkylation of isobutane by olefins (see Sec. 4.5).

Fuel of a required quality is produced by mixing the compounds obtained with other hydrocarbons and various additives.

The antidetonation properties of fuel can be enhanced by adding some substances to it. The most important additive is tetraethyllead $Pb(C_2H_5)_4$ (TEL). In technological processes, a mixture which contains this additive is called *ethyl fluid*, while gasoline to which this fluid is added is known as ethylated gasoline. Ethyl fluid consists of 63 per cent of $Pb(C_2H_5)_4$, 26 per cent of dibromoethane $CH_2Br—CH_2Br$, 9 per cent of dichloroethane $CH_2Cl—CH_2Cl$, and a dye. An addition of 1-2 ml of TEL per litre of gasoline raises the octane number by 8-10 units, but it is not recommended to add large amounts of this fluid. When the fuel burns, lead is isolated as oxide, whose deposition on the walls of the engine puts it out of order. Dibromoethane and dichloroethane which are added to tetraethyllead turn lead oxide into volatile lead halides, which are ejected from the cylinder together with exhaust fumes. It follows that engines running on ethylated gasoline produce a poisonous exhaust. Tetramethyllead $Pb(CH_3)_4$ and other organometallic compounds are used more commonly in modern engines having a high compression ratio.

Diesel fuel contains unbranched and slightly branched high-boiling hydrocarbons (kerosene-gas oil fraction). The quality of this fuel is determined by the cetane scale and is characterized by the *cetane number*. The number 100 stands for the flammability of cetane (*n*-hexadecane $C_{16}H_{34}$), and 0, for the flammability of α-methylnaphthalene. Diesel fuel having the cetane number of 50-60 is usually used.

Jet engines use the most diverse fuel, usually *n*-alkanes whose boiling point is up to 315°C.

PART II

COMPOUNDS WITH HOMOGENEOUS FUNCTIONS

Compounds having homogeneous functions are organic compounds which contain one or several identical functional groups in the molecule.

Chapter 9

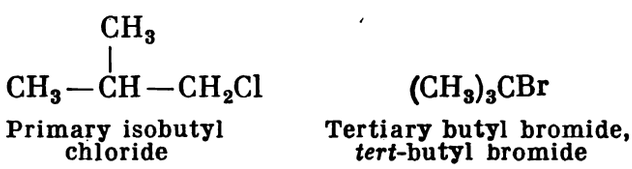
HALOGEN DERIVATIVES

The derivatives of hydrocarbons, in which one or more hydrogen atoms are replaced by a halogen, are called *halogen derivatives*. Fluoro-, chloro-, bromo- and iodo-derivatives are known. A distinction is made between mono-, di- and polyhalogen derivatives, depending on the number of halogen atoms.

For monohalogen derivatives, general names are also used; for example, alkane derivatives are called *alkyl halides* or halogen alkanes; the derivatives of cycloalkanes, *cycloalkyl halides*, and the derivatives of aromatic compounds containing a halogen which is attached directly to the carbon atom of the ring, *aryl halides*.

9.1. Isomerism. Nomenclature. Alkyl halides have the general formula of $C_nH_{2n+1}X$ (where X = F, Cl, Br, I). The isomerism of halogen derivatives is engendered by the isomerism of the carbon skeleton and the position of a halogen.

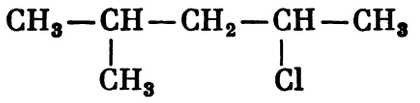
The rational names of halogen derivatives are usually composed from the name of the hydrocarbon radical and the corresponding halogen. Alkyl halides may be divided into primary, secondary, and tertiary halides, depending on the carbon atom which has a halogen, e.g.,



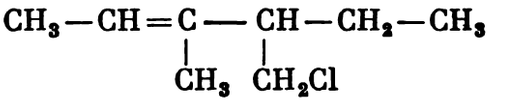
Primary isobutyl chloride — Tertiary butyl bromide, *tert*-butyl bromide

In modern international nomenclature, the name of a halogen and the numeral which indicates its position are placed in front of the name of the hydrocarbon. The selection of the principal chain and

its numeration are determined by the functional group, which is a halogen in this case, e.g.,



2-Chloro-4-methylpentane

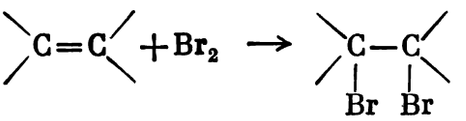


1-Chloro-3-methyl-2-ethyl-3-pentene

9.2. Preparation of Halogen Derivatives. Preparation of saturated halogen derivatives. 1. Direct halogenation of alkanes (chlorination or bromination) was considered earlier as a typical example of a radical chain reaction. It is difficult to practically use this reaction, because position isomers, mono- and polysubstituted products, are always formed when it is being carried out. Nevertheless, the reaction is important industrially, since the mixtures are often used without separation or individual substances are isolated by fractional distillation.

The substitution reaction in cycloalkanes occurs similarly.

2. The action of chlorine or bromine on alkenes. This reaction causes the formation of dihalogenated paraffins (see Sec. 4.5):



3. The addition of hydrogen halides to alkenes, as a result of which alkyl halides are formed:

$$CH_2=CH-R+HBr \longrightarrow CH_3-CHBr-R$$

This reaction of electrophilic addition was described earlier (see Sec. 4.5).

4. The action of hydrogen halides or halogen derivatives of phosphorus on alcohols:

$$ROH+HBr \longrightarrow RBr+H_2O$$
$$ROH+PCl_5 \longrightarrow RCl+HCl+POCl_3$$

To obtain iodine derivatives, it is necessary to take alcohol, free iodine and red phosphorus:

$$3I_2+2P \longrightarrow 2PI_3$$
$$3ROH+PI_3 \longrightarrow 3RI+H_3PO_3$$

Since alcohols are readily available, this reaction is used often for obtaining alkyl halides.

Preparation of unsaturated halogen derivatives. 1. The thermal chlorination of ethylene (300-600°C) causes the formation of vinyl chloride:

$$CH_2=CH_2+Cl_2 \xrightarrow{300-600^\circ C} CH_2=CHCl+HCl$$

In the thermal halogenation of ethylene homologues, hydrogen in the allylic position is replaced (see Sec. 4.5):

$$CH_2=CH-CH_3+Cl_2 \xrightarrow{500^\circ C} CH_2=CH-CH_2Cl+HCl$$

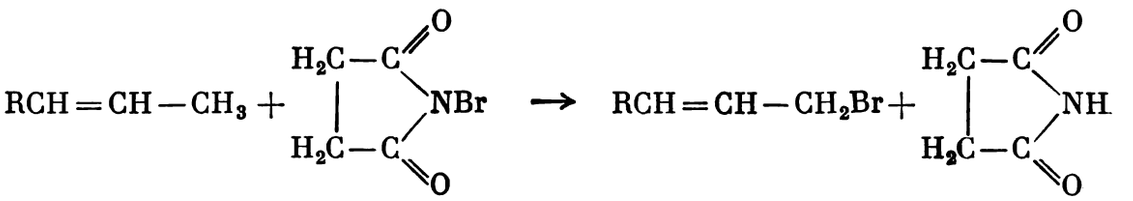
2. The dehydrohalogenation of polyhalogen derivatives as they are heated with an alcoholic solution of alkali or as their vapours are passed over a heated catalyst (activated charcoal, alumina, 300°C) causes the formation of compounds containing a halogen at the double bond:

$$CH_2Cl-CH_2Cl \xrightarrow[-HCl]{} CH_2=CHCl$$

3. The addition of hydrogen chloride to alkynes:

$$CH\equiv CH+HCl \xrightarrow{160^\circ C;\ HgCl_2} CH_2=CHCl$$

4. The bromination in the allylic position. The interaction between alkenes or cycloalkenes and halogen carriers, particularly N-bromosuccinimide (Ziegler reaction, 1942):



N-Bromosuccinimide Succinimide

The method is widely used in the laboratory.

5. The addition of hydrogen halides to compounds with conjugated double bonds. In this case, a mixture of the products of 1,2- (*a*) and 1,4-addition (*b*) is formed:

$$CH_2=CH-CH=CH_2+HCl \begin{cases} \xrightarrow{a} CH_3-CHCl-CH=CH_2 \\ \xrightarrow{b} CH_3-CH=CH-CH_2Cl \end{cases}$$

The mechanism of this reaction is considered in Sec. 6.2.

Preparation of aromatic halogen derivatives. When a halogen acts on aromatic compounds, different products are formed, depending on the reaction conditions.

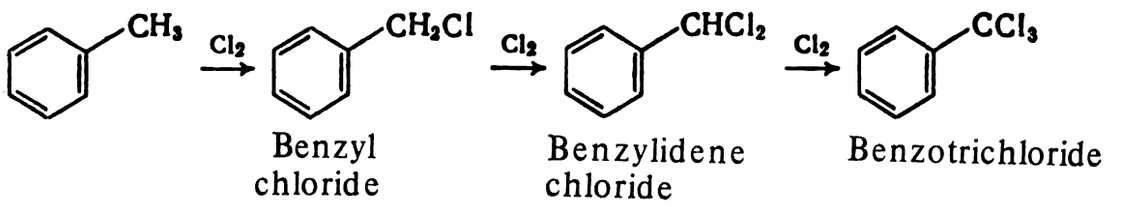
(a) In the presence of catalysts (halides of iron, aluminium, etc.) and at room temperature, hydrogen undergoes electrophilic substitution in the benzene ring (see Sec. 7.5):

$$C_6H_6+Br_2 \xrightarrow{(Fe,\ FeBr_3)} C_6H_5Br+HBr$$

The action of excess halogen can cause the formation of di- and polyhalogenated products even until all the hydrogen atoms of the

ring are replaced (C_6Cl_6, hexachlorobenzene; $C_6Cl_5CH_3$, pentachlorotoluene).

(b) When there is no catalyst, a radical reaction of substitution in the side chain occurs as benzene homologues are heated or illuminated. Mono- and polyhalogen derivatives can be obtained, depending on the amount of a halogen. For example, when toluene is chlorinated under these conditions, the following compounds can be obtained:



Benzyl chloride — Benzylidene chloride — Benzotrichloride

(c) In the case of intense lighting (by means of ultraviolet light of the mercury lamp) without oxygen, benzene adds a halogen and then cyclohexane derivatives are formed:

$$C_6H_6 \xrightarrow{Cl_2} C_6H_6Cl_6$$

Benzene — Hexachlorocyclohexane

A very important reaction for obtaining aryl halides is the substitution of a halogen for the diazo group in diazonium salts (see Sec. 16.2).

9.3. Physical Properties. Table 9.1 gives the physical properties of some halogen derivatives.

As Table 9.1 shows, the first members of the alkyl halide and alkenyl halide series have low boiling points. The boiling point rises as the radical in the homologous series and the atomic number of a halogen grow. Iodine derivatives have the highest boiling points. The lower members of the homologous series possess higher density, among them, iodine derivatives have the highest density. Aliphatic chlorides are lighter than water, while bromides and iodides are heavier. Density decreases as the hydrocarbon radical increases.

Most halogen derivatives are colourless liquids having a peculiar odour; polyiododerivatives are yellow solids. All the halogen derivatives are practically water-insoluble, but are soluble in organic solvents, i.e., hydrocarbons, alcohols and ether; they are insoluble in concentrated sulphuric acid, and therefore impurities of alcohols and ether can be removed by shaking them with sulphuric acid, in which the impurities dissolve.

Some alkyl halides act as an anesthetic. For example, ethyl chloride is used for local anesthesia, while chloroform, for general anesthesia. Iodoform CHI_3 possesses antiseptic properties.

TABLE 9.1. **Physical Properties of Some Halogen Derivatives**

Names of radicals	Formulas of radicals	Chloride		Bromide		Iodide	
		b. p., °C	d_4^{20}	b. p., °C	d_4^{20}	b. p., °C	d_4^{20}
Methyl	CH_3—	—24.2	0.92	4.3	1.7	42.3	2.27
Ethyl	C_2H_5—	+13	0.9	38.4	1.43	72.3	1.93
Propyl	C_3H_7—	46.4	0.89	70.9	1.35	102	1.74
Isopropyl	$(CH_3)_2CH$—	36.5	0.86	59.5	1.32	89.4	1.70
Vinyl	$CH_2=CH$—	—14	—	15.8	—	56	—
Allyl	$CH_2=CH-CH_2$—	+45.7	0.93	70	—	102	1.84
Phenyl	C_6H_5—	132	1.10	155	1.49	189	1.83
Benzyl	$C_6H_5CH_2$—	179	1.09	198	1.43	96	1.73
Benzylidene	$C_6H_5CH<$	205	1.25	—	—	—	—

The derivatives of aromatic hydrocarbons which contain a halogen in the side chain at the carbon atom attached to the aromatic ring have an irritating odour and are toxic. Some of them, such as benzyl bromide $C_6H_5CH_2Br$, were used in World War I as tear-producing poisonous substances called lacrimators (from the Latin word "lacrima", meaning "tear").

9.4. Chemical Properties. Nucleophilic substitution reactions. In halogen derivative molecules, the halogen atom is more electronegative than the carbon atom, and the carbon-halogen bond is polarized:

$$>\overset{|}{C}-\overset{\delta+\ \delta-}{X} \quad (X=Cl,\ Br,\ I)$$

The nucleophilic reagent, while attacking the halogen derivative molecule, forms a bond with the carbon atom, which possesses reduced electron density, and forces out the halogen atom from the molecule. As a result of the reaction, the halogen is replaced by a nucleophilic group. Such reactions are called **nucleophilic substitution** reactions and are denoted by S_N.

In nucleophilic substitution, reactions can occur according to two different mechanisms, which are known as the S_N2 **(bimolecular nucleophilic substitution)** and S_N1 **(unimolecular nucleophilic substitution).** The numerals indicate the **molecularity** of the reaction.

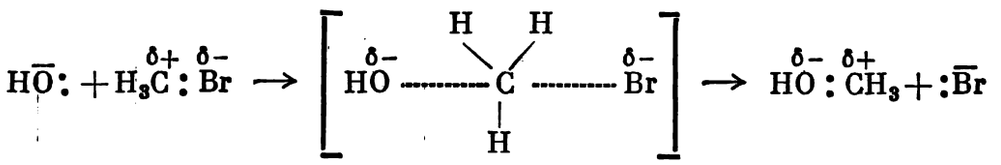
The *bimolecular reaction* in its general form can be written as:

$$\bar{Y}:+\overset{\delta+\ \delta-}{R}:X \rightleftarrows \overset{\delta-\ \delta+}{Y}:R+:\bar{X}$$

Both reagents participate at the rate-determining stage of the reaction and if they are in commensurable concentrations (without

a large excess of either of them), the rate of the S_N2 reaction is proportional to the concentration of both reagents.

In the hydrolysis of alkyl halides, the bimolecular reaction is a single-stage process engendering a *transition complex* or, in other words, a *transition state*. A typical example of such a reaction is the hydrolysis of methyl bromide:



Transition state

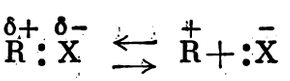
The hydroxyl ion can approach the carbon atom only from the side opposite to that where the bromine atom is located. The approximation of the hydroxyl ion to the carbon atom, the removal of bromine and its conversion into the bromide ion are processes which occur simultaneously. The negative charge in the transition complex is distributed between the entering and leaving nucleophilic groups.

The readiness with which the nucleophile approaches the molecule is important in effecting the reaction by S_N2 mechanism. The structure of an alkyl halide is also of great importance: primary alkyl halides react more rapidly than secondary ones, and the more so than tertiary halides. The given series of alkyl halides is arranged according to the decrease of the rate of S_N2 reactions:

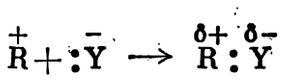
$$CH_3X > CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$$

The *monomolecular reaction* is a two-stage ionic process. In general, it can be written as:

first stage, reagent ionization and the formation of the carbonium ion:



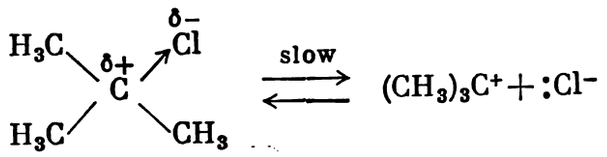
second stage, the interaction between the carbonium ion and the nucleophilic particle:



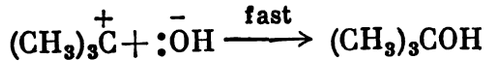
The reaction rate depends on the concentration of either of the reagents. It is determined by dissociation and the formation of the carbonium ion.

In the hydrolysis of alkyl halides, their ionization and the formation of the carbonium ion occur under the action of a polar solvent, which promotes the reaction according to S_N1 mechanism, the reaction proceeds better in an alkaline medium. Let us consider this process by taking the example of *tert*-butyl chloride.

First stage, the ionization of *tert*-butyl chloride and the formation of the *tert*-butyl carbonium ion:



Second stage, the reaction between the carbonium ion and the hydroxyl ion:

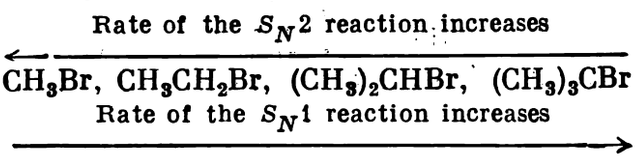


As a rule, the rate of a multistage process is determined by the slowest stage, the first one in this case.

The accumulation of alkyl groups at the carbon atom stabilizes the carbonium ion and thus promotes the reaction according to S_N1 mechanism; such reactions are characteristic of tertiary alkyl halides.

Secondary alkyl halides can react according to S_N1 or S_N2 mechanism, depending on the reaction conditions.

The direction of the change in the rate of the S_N2 and S_N1 reactions is shown in the alkyl bromide series given below:



In many nucleophilic substitution reactions, the reagent is a solvent: in hydrolysis, it is water; in alcoholysis, alcohol; in acetolysis, acetic acid, and in ammonolysis, ammonia.

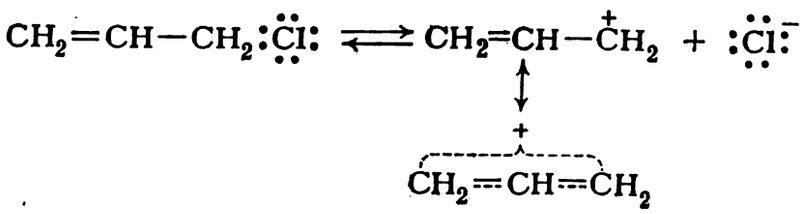
Effect of the hydrocarbon radical on the properties of a halogen in halogen derivatives. The mechanism of the nucleophilic substitution reaction and the reactivity of halogen derivatives depend on the nature of a halogen and on that of the hydrocarbon radical linked with it, on the nature of the reagent, and on the solvent and the reaction conditions: temperature, catalyst, etc.

The reactivity of various types of alkyl halides was considered earlier.

Halogen cycloalkanes are similar by their behaviour to secondary alkyl halides. In most cases, they react according to S_N1 mechanism, but the reaction rate depends also on the length of the ring. The reaction for rings having five or more carbon atoms occurs well, while the derivatives of cyclopropane are similar to vinyl halide.

The properties of a halogen in unsaturated halogen derivatives depend on the mutual arrangement of the halogen atom and the double bond. A halogen in an *allylic position* with respect to the double bond, like in allyl chloride $CH_2=CH-CH_2Cl$, is more active than in saturated compounds because of the high stability

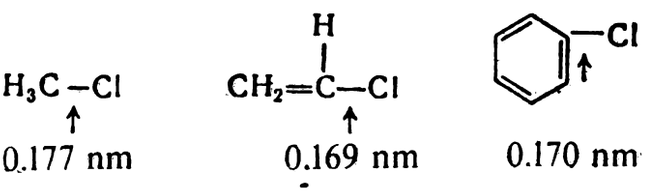
of the carbonium ion owing to *conjugation*:



Therefore, the reaction according to the S_N1 mechanism occurs more readily for allyl chloride than for alkyl halides.

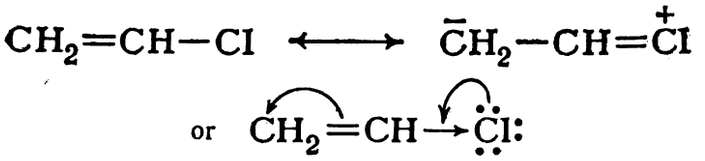
Compounds of the type of benzyl chloride, $C_6H_5CH_2Cl$, and triphenyl chloromethane, $(C_6H_5)_3CCl$, also readily form carbonium ions, which are stabilized by *conjugation*, and therefore substitution reactions according to the S_N1 mechanism occur more readily for them than for saturated halogen derivatives. If a halogen is remote from the double bond or from the benzene ring by two or more carbon atoms, halogen activity in such compounds is similar to that in alkyl halides.

Compounds containing a halogen attached to the double bond (such as vinyl halide) are poorly active. The carbon-halogen bond is shorter than usual in this case. This is also true of aromatic compounds which are substituted by a halogen in the ring:



0.177 nm 0.169 nm 0.170 nm

The halogen atom in these compounds is conjugated at the expense of its free electrons with the π-electrons of the double bond or with the aromatic sextet. As a result, the C—X bond is *partially double-bonded*, and this reduces the length of the bond and increases its energy. For example, the structure of vinyl chloride can be shown most precisely by two extreme formulas or one mesomeric formula:



Conjugation reduces the polarity of the C—Cl bond and thus worsens the conditions for nucleophilic substitution reactions. The conditions of hydrolysis of some halogen-derivative hydrocarbons

that characterize the mobility of a halogen in these compounds are given below:

	Hydrolysis
Chloroalkanes, chlorocycloalkanes . .	By aqueous alkaline solutions on boiling
Allyl chlorides, benzyl chlorides . .	By an excess of water on boiling
Triphenyl chloromethane	By water in the cold

Compounds of the type of vinyl chloride, $CH_2=CHCl$, and phenyl chloride, C_6H_5Cl, are not hydrolyzed under these conditions: they contain an "unsaponifiable" halogen. Under more severe conditions, they also enter into nucleophilic substitution reactions.

In compounds having the same radical, reactivity increases in the series:

$$RCl < RBr < RI$$

Reactions of nucleophilic substitution of a halogen are often accompanied by reactions of elimination of hydrogen halide with the formation of alkenes. This is observed especially frequently in reactions when the intermediately formed carbonium ion is converted into a stable product as a result of proton elimination and not anion addition, e.g.,

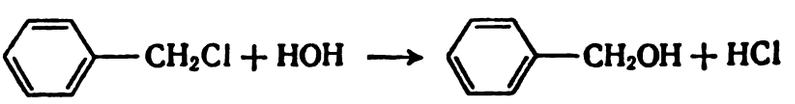
$$CH_3-CH_2-CH_2Cl \rightarrow CH_3-CH_2-\overset{+}{C}H_2+Cl^-$$

$$CH_3-CH_2-\overset{+}{C}H_2 \xrightarrow[-H^+]{} CH_3-CH=CH_2$$

Elimination reactions are accelerated in a strongly basic medium on heating.

Most important reactions of halogen derivatives. 1. Hydrolysis (in an alkaline or acid medium). Monohalogen derivatives yield alcohols as a result of hydrolysis, e.g.,

$$RX+HOH \rightarrow ROH+HX$$



Benzyl alcohol

Aldehydes or ketones are formed in the hydrolysis of polyhalogen derivatives containing two halogen atoms attached to one carbon atom (see Sec. 11.2), and acids are formed in the hydrolysis of similar trihalogen derivatives (see Sec. 12.2). The hydrolysis of polyhalogen derivatives, whose halogen atoms are attached to different carbon

atoms, causes the formation of polyhydric alcohols:

$$ClCH_2—CH_2Cl+2HOH \rightarrow \underset{\text{Ethylene glycol}}{HOCH_2—CH_2OH}+2HCl$$

2. The exchange of a halogen for the alkoxy group OR in a reaction with alkali-metal alkoxides. In this case, ethers are formed:

$$CH_3—CH_2Br+NaOCH_3 \rightarrow CH_3—CH_2—O—CH_3+NaBr$$

3. The exchange of a halogen for the nitrile group: the formation of nitriles in a reaction with potassium cyanide. In this case, the carbon chain is built up (see Sec. 12.25):

$$CH_3—CH_2I+KCN \rightarrow \underset{\text{Propionitrile}}{CH_3—CH_2—CN}+KI$$

Nucleophilic substitution reactions can be used to obtain also nitro compounds RNO_2 (Sec. 14.2), amines RNH_2 (Sec. 15.2), thiols RSH (Sec. 13.1), and others from halogen derivatives.

Among other reactions of halogen derivatives, of great importance are the above-mentioned elimination of hydrogen halides from these derivatives with the formation of olefins and acetylenes, the synthesis of the homologues of benzene in alkylation by the Friedel-Crafts reaction, and the synthesis of paraffins by the Würtz reaction.

Aryl halides undergo electrophilic substitution reactions like aromatic hydrocarbons. A halogen, being an *ortho-para*-directing group, deactivates the ring (see Sec. 15.6).

The reaction of the formation of organomagnesium compounds is especially important (see Sec. 17.2). It occurs practically with any halogen derivatives, regardless of the nature of the organic radical:

$$RI+Mg \xrightarrow{\text{ether}} RMgI$$

Halogen derivatives are rather stable with respect to oxidizing agents. Reducing agents convert them into hydrocarbons, e.g.,

$$C_8H_{17}I+HI \rightarrow C_8H_{18}+I_2$$

9.5. Important Individual Halogen Derivatives. Practically the most important halogen derivatives are chlorine derivatives, because chlorine is a cheap and the most easily available agent of halogenation. In the laboratory, bromine derivatives are used more often owing to their higher reactivity and to the convenience of obtaining them (liquid bromine instead of chlorine gas).

Methyl chloride, CH_3Cl, is a gas whose b.p. is —24.2°C. It is produced industrially by thermally chlorinating (400°C) methane. Under these conditions, other chlorine derivatives of methane are formed as impurities. To reduce the formation of polychlorinated products, the reaction is carried out in the presence of a large excess of methane. Methyl chloride is obtained also from methyl alcohol

and hydrogen chloride under pressure, and is preserved in pressurized steel cylinders. It is used as a methylating agent and as a refrigerant.

Ethyl chloride, C_2H_5Cl, b.p. 13°C. It is produced industrially by hydrochlorinating ethylene in the presence of catalysts ($FeCl_3$, $AlCl_3$). It is obtained also from ethyl alcohol under the action of hydrogen chloride, and by chlorinating accompanying oil gas. Ethyl chloride is used in syntheses as an ethylating agent. Since ethyl chloride has a low boiling point and evaporates rapidly, it is employed as a local anesthetic for minor surgeries. It is mainly used to produce tetraethyl lead $(C_2H_5)_4Pb$ (see Sec. 8.1).

Dichloroethane (*ethylene dichloride*), $CH_2Cl—CH_2Cl$, is a colourless liquid whose b.p. is 84°C, and d_4^{20}, 1.25. It is a good solvent for fats, oils, paraffins, resins, waxes, rubber, and other products, and also for many inorganic substances, such as sulphur, phosphorus and iodine. It is widely used as a solvent, e.g., in removing paraffin from oil products, in scouring wool and fur, degreasing metallic parts, etc. It is employed for synthesizing vinyl chloride, and also ethylene glycol $HOCH_2—CH_2OH$ (see Sec. 10.6).

The vapours of ethylene chloride are toxic, and therefore care must be taken in handling it. It is prepared industrially mainly by chlorinating ethylene (see Sec. 4.5).

Chloroform (*trichloromethane*), $CHCl_3$, is a colourless liquid having a characteristic sweet odour; its b.p. is 62°C, and d_4^{20}, 1.48.

In hydrolysis, chloroform yields formic acid, and hence its name. Chloroform is a good solvent for fats, resins and rubber. It is a strong anesthetic. It was the first organic compound used (1848) for general narcosis in surgeries. At present, it is employed rarely for narcosis, owing to an undesirable side effect on the organism.

Chloroform is oxidized in the air, and phosgene, $COCl_2$, a very toxic substance, is among the oxidation products. On storage, the formation of phosgene can be precluded by adding alcohol (up to 1 per cent) to chloroform.

Chloroform is obtained industrially under the action of chlorinated lime on ethyl alcohol (see Sec. 11.5).

Carbon tetrachloride (*tetrachloromethane*), CCl_4, is a colourless liquid; its b.p. is 76.5°C, and d_4^{20}, 1.59. It is a good solvent for rubber, fats, oils, resins, etc. It is nonflammable and is used in fire extinguishers to put out fires in laboratories and book depositories, but it is dangerous to employ these fire extinguishers in closed premises because of the phosgene formed. Carbon tetrachloride is used industrially as a solvent, and it is employed for chemically cleaning clothes and carrying out various syntheses.

Carbon tetrachloride is obtained from carbon disulphide and chlorine:

$$CS_2 + 3Cl_2 \xrightarrow{SbCl_3,\ 70°C} CCl_4 + S_2Cl_2$$

Vinyl chloride, $CH_2=CHCl$, is a colourless gas whose b.p. is —13.9°C. It is preserved in pressurized steel cylinders. Vinyl chloride is an important monomer for producing *polyvinyl chloride* (see Sec. 23.4). It is produced industrially in large amounts. Its raw material is ethylene or acetylene.

Ethylene is chlorinated to obtain dichloroethane, from which hydrogen chloride is eliminated under the action of a solution of alkali in methyl alcohol:

$$CH_2=CH_2 \xrightarrow{Cl_2} ClCH_2—CH_2Cl \xrightarrow[-HCl]{CH_3OH;\ NaOH} CH_2=CHCl$$

Another way of converting dichloroethane into vinyl chloride is by pyrolysis at 400-500°C over activated charcoal or pumice. But vinyl chloride obtained by this method is of lower purity.

Vinyl chloride can be obtained from acetylene and hydrogen chloride by carrying out the reaction in a liquid phase, i.e., by passing both gases at 60°C into a solution of a catalyst which consists of cuprous and ammonium chlorides. The vapour-phase method is more commonly used. The reaction between acetylene and hydrogen chloride is carried out at 150°C over activated charcoal on which mercuric chloride, $HgCl_2$, is deposited.

Trichloroethylene (1,1,2-*trichloroethene*), $CHCl=CCl_2$, is a colourless liquid whose b.p. is 87°C, and d_4^{20}, 1.4. It is obtained by chlorinating acetylene and subsequently dehydrochlorinating the tetrachloroethane formed (by boiling it with lime):

$$CH\equiv CH \xrightarrow{2Cl_2} CHCl_2—CHCl_2 \xrightarrow{HCl;\ Ca(OH)_2} CHCl=CCl_2$$

Tetrachloroethane and trichloroethylene are very good solvents of fats, sulphur, etc. An advantage of trichloroethylene over other solvents is that it does not corrode the apparatus too much, and therefore it is widely used in technological processes.

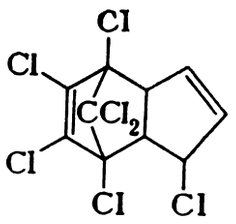
Chlorobenzene, C_6H_5Cl, is a colourless liquid whose b.p. is 132°C, and d_4^{20}, 1.06. It is produced industrially by the chlorination of benzene in the presence of the $FeCl_3$ catalyst (Sec. 7.5) or by oxidizing chlorination. In the latter method, a mixture of vapours of benzene, hydrogen chloride and air is passed over a heated catalyst, cuprous chloride:

$$C_6H_6+{}^1/_2O_2+HCl \xrightarrow{Cu_2Cl_2} C_6H_5Cl+H_2O$$

Chlorobenzene is an important intermediate for synthesizing various substances (phenol, etc.), although chlorine is poorly active in it. It is produced industrially in large amounts.

Polychlorine derivatives are used as insecticides in agriculture. For example, *heptachlor* I is used to combat the beet pest, and

hexachlorobutadiene II, grape pests:



I

$$Cl_2C=CCl-CCl=CCl_2$$

II

Until recently, the insecticide DDT (4,4′-dichlorodiphenyltrichloroethane) was widely used in all countries. At present, an effort is made to limit the application of DDT and other chloro-organic insecticides, because they are very stable and can be detrimental to useful insects, animals and Man if they are used carelessly.

9.6. Fluorine Derivatives. Fluorine derivatives of hydrocarbons differ from other halogen derivatives by their properties and by the methods of their preparation. The specific features of fluorine compounds are determined above all by the properties of the fluorine element itself.

Preparation. Hydrocarbons cannot be fluorinated directly, because they ignite in a fluorine atmosphere. The process is sometimes accompanied by an explosion, and the reaction is highly exothermic. Much energy is liberated, a part of it being consumed for rupturing the carbon bonds, and therefore the organic substance disintegrates.

Although it is difficult to obtain fluorine derivatives, many methods of synthesizing them have been worked out, because these substances are now of paramount importance in modern technological processes owing to their valuable properties. The most important industrial methods of obtaining fluoroorganic compounds are the following:

1. Catalytic fluorination of hydrocarbons. A mixture of hydrocarbon vapours and nitrogen is passed through a layer of a heated catalyst, cobalt trifluoride:

$$R-H+2CoF_3 \xrightarrow{300°C} R-F+2CoF_2+HF$$

Cobalt trifluoride is reactivated by fluorinating the cobalt difluoride formed:

$$2CoF_2 \xrightarrow{F_2;\ 250°C} 2CoF_3$$

All the hydrogen atoms in hydrocarbons can be replaced and *perfluorohydrocarbons* (or *fluorocarbons*) can be obtained in this way. The prefix *per-* means that all the hydrogen atoms are replaced e.g., CF_4 and C_2F_6 (perfluoromethane and perfluoroethane).

2. An advanced method of fluorination is "jet" fluorination. Fluorine is fed through an opening into a special burner, and an

organic compound diluted with an inert gas is fed through another. The mixture burns smoothly, and fluorinated products having the same carbon skeleton are formed.

3. Action of hydrogen fluoride on alkenes:

$$CH_2=CH_2+HF \rightarrow CH_3-CH_2F$$

4. Wide use is made of the method of obtaining mixed fluorochloroalkanes from polychloride derivatives under the action of hydrogen fluoride or antimony trifluoride in the presence of antimony pentachloride, $SbCl_5$:

$$CCl_4+2HF \rightarrow CF_2Cl_2+2HCl$$
$$3CCl_4+2SbF_3 \rightarrow 3CF_2Cl_2+2SbCl_3$$

Antimony trifluoride is reactivated under the action of hydrogen fluoride from the antimony trichloride formed.

5. Fluorinated olefins can be obtained by pyrolyzing defluorochloromethane (700-1000°C):

$$2CHF_2Cl \rightarrow \underset{\text{Tetrafluoroethylene}}{CF_2=CF_2}+2HCl$$

About 35-40 years ago, only a few fluorocarbons were known, but now thousands of fluoroorganic compounds are known, and this field of chemistry is developing rapidly.

Properties of fluoroorganic compounds. Fluorocarbons have a lower boiling point and are more volatile than the corresponding alkanes. For example, *n*-heptane has a boiling point of 98°C, and perfluoroheptane, 82°C. Fluorine atoms have a stabilizing effect on other halogen atoms in a molecule. For example, chlorine is not hydrolyzed in difluorodichloromethane.

Fluorocarbons are nonflammable, and they are characterized by thermal stability (up to 400°C) and high chemical inertness with respect to the action of acids and alkalies. Fluorine atoms in perfluorocompounds create a dense barrier around the carbon atom, protecting the carbon skeleton from the effect of other reagents.

Fluorine is more electronegative than oxygen, and therefore fluorocarbons are stable toward oxidizing agents. Molten metallic sodium decomposes them only at 400°C. High-molecular-weight perfluorocarbons are similar to noble metals by their chemical stability and even excel them in this respect.

Important representatives and their use. *Dichlorodifluoromethane* (*Freon*-12), CF_2Cl_2, is a colourless gas having a b.p. of —30°C. It is widely used as a coolant in deep-freeze refrigerators, domestic refrigerators and air conditioners. Freon-12 is widely used as a propellant (low-boiling solvent) for obtaining aerosols. At present, the aerosol method is used for spraying toxic chemicals, lacquers, paints, etc.

Bromotrifluoromethane, *dibromodifluoromethane* and 1,2-*dibromotetrafluoroethane* are used as fire-extinguishing liquids for fire extinguishers in jet planes, and for extinguishing liquid rocket fuel. They are less toxic than CCl_4.

Tetrafluoroethylene, $CF_2=CF_2$, is a colourless gas whose b.p. is —78°C and m.p., —142°C. It is produced industrially from chloroform and hydrogen fluoride with the subsequent pyrolysis (700-1000°C) of intermediate chlorodifluoromethane:

$$CHCl_3+2HF \rightarrow CHF_2Cl+2HCl$$

$$2CHF_2Cl \xrightarrow[-2HCl]{} CF_2=CF_2$$

Tetrafluoroethylene is readily polymerized in the presence of peroxides into polytetrafluoroethylene, or Teflon.

Chlorotrifluoroethylene, $CF_2=CFCl$, is a colourless gas having a boiling point of —27°C. It is obtained by dechlorinating trichlorotrifluoroethane:

$$CF_2Cl-CFCl_2 \xrightarrow{Zn} CF_2=CFCl+ZnCl_2$$

The polymer of trifluorochloroethylene is prepared on its basis (see Sec. 23.4).

9.7. Inductive Effect. It is very important to take account of the *mutual effect of atoms in a molecule* when studying the structure and properties of organic compounds and individual functional groups.

The concepts of the mutual effect of atoms which are directly linked as well as those not linked were first stated by A. M. Butlerov (1861) and evolved by his pupil V. V. Markovnikov (1869). Markovnikov drew also the conclusion that the effect of an element on other elements weakens as elements move away from one another in the common chain of bonded atoms. These concepts were evolved further in the electronic theory (by Ingold and others).

When the σ-bond is being formed between atoms with different electronegativity, the electron density in the molecule is displaced towards the atom which is more electronegative. This polarizes the molecule and causes the formation of partial charges (see Sec. 1.8). For example, electron density is displaced towards chlorine in the methyl chloride molecule, and this can be expressed by the formulas:

$$H_3C \dashrightarrow Cl \quad \text{or} \quad \overset{\delta+}{CH_3}—\overset{\delta-}{Cl}$$

If the chlorine atom is bonded with carbon of a saturated chain, such as in chloropropane, the electron density is displaced further along the σ-bonds of carbon atoms:

$$H_3\overset{3}{C} \rightarrow \overset{2}{C}H_2 \rightarrow \overset{1}{C}H_2 \rightarrow Cl$$

The atom C-1, which is short of electrons, will withdraw them from C-2, while C-2, from C-3. But the effect of the chlorine atom on C-1 is greater than that of C-1 on C-2, while the latter effect is greater than that of C-2 on C-3, and the portion of the partial charge (δ^+), which characterizes electron insufficiency, diminishes:

$$\overset{\delta'''+}{CH_3}—\overset{\delta''+}{CH_2}—\overset{\delta'+}{CH_2}—Cl \quad \delta'+ > \delta''+ > \delta'''+$$

The displacement of electron density along the σ-bonds in a molecule is known as *inductive polarization* or the *inductive effect* (I-effect). The inductive effect is caused by the tendency of the atom or a group of atoms to give or take away electrons. The inductive displacement of electron density is *effected in one direction along the saturated chain* (σ-electron displacement) and *is not accompanied by a transfer of electrons from the shell of one atom into that of another*. The inductive effect rapidly dies away.

If electron density is displaced towards the substituent (e.g., chlorine), such a substituent is called an *electron acceptor*, while the effect it causes is said to be *negative* and is denoted by "—I". But if the effect of a group increases electron density at the neighbouring carbon atom, i.e., if the group repels electrons (e.g., the methyl radical), such a substituent is called an *electron donor*, while the effect it causes is said to be *positive* and is denoted by "+I".

A typical example of the —I effect is the effect of a halogen in the halogen-substituted products of carboxylic acids on their acidity (see Sec. 18.1). As for the role of electronic effects in substitution in the aromatic nucleus, see Sec. 15.6.

Chapter 10

HYDROXYL COMPOUNDS AND THEIR DERIVATIVES

The products of replacement of hydrogen in hydrocarbons by the hydroxyl group (hydroxy group) are known as *alcohols*. The general formula of alcohols is R—OH.

The hydroxyl derivatives of aromatic hydrocarbons are called *aromatic alcohols* when the hydroxyl group is in the side chain, and *phenols* when the hydroxyl group is attached directly to a benzene ring.

Aliphatic alcohols are divided into *saturated* and *unsaturated* ones in conformity with the nature of the hydrocarbon radical. There are the following types of alcohol, depending on the number of hydroxyl groups in the molecule:

monohydric alcohols

$CH_3—CH_2OH$	$CH_2=CH—CH_2OH$	$C_6H_5—CH_2OH$
Ethyl alcohol	Allyl alcohol	Benzyl alcohol

dihydric alcohols

$HOCH_2—CH_2OH$	$CH_3—CH(OH)—CH_2OH$
Ethylene glycol	Propylene glycol

trihydric alcohols

$HOCH_2—CH(OH)—CH_2OH$

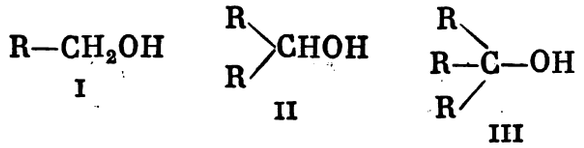
Glycerol

The carbon atom is capable of firmly retaining only one hydroxyl group; the hydroxyl cannot be attached also to a multiple carbon bond, although there are exceptions to these rules.

MONOHYDRIC ALCOHOLS

10.1. Isomerism. Nomenclature. The **isomerism of alcohols** is caused by the structure of the radical (isomerism of the carbon skeleton) and the position of the hydroxyl (position isomerism). There are *primary* I, *secondary* II and *tertiary* III alcohols in conformity with the position of the hydroxyl in the molecule, depending on the carbon atom (the primary, secondary or tertiary one) with which

it is linked:

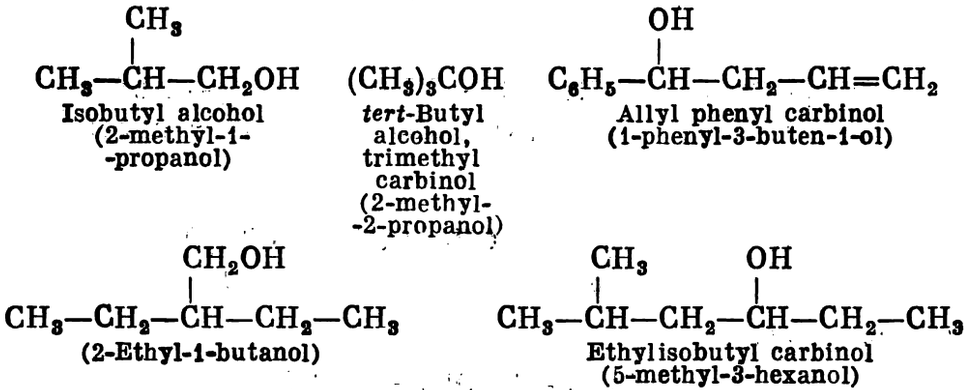


I II III

Nomenclature. The *rational* nomenclature of alcohols is widely used. A name is derived from the appropriate hydrocarbon radical in combination with the word "alcohol". This is convenient for simple radicals: methyl alcohol CH_3OH or isopropyl alcohol $CH_3—CHOH—CH_3$. Alcohol which is more complex by its structure can be regarded as a derivative of methyl alcohol, or carbinol (*carbinol* nomenclature).

By modern international rules, the suffix **ol** and a numeral indicating the number of the carbon atom to which the hydroxyl is attached are added to the name of a hydrocarbon. The carbon atom to which the hydroxyl is attached is necessarily included in the principal chain, and it begins the numeration; the *function* determines the selection of the principal chain.

Several examples are given below (the trivial or carbinol name is given directly under the formula, while the name accepted in international nomenclature is given in parentheses):



Isobutyl alcohol (2-methyl-1-propanol)

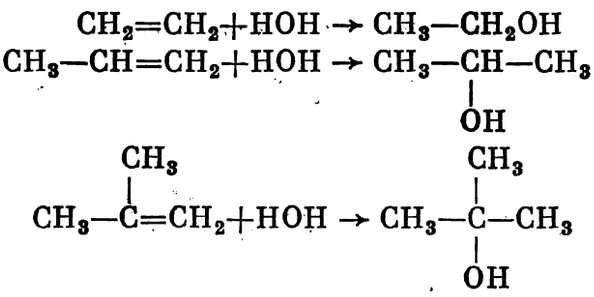
tert-Butyl alcohol, trimethyl carbinol (2-methyl-2-propanol)

Allyl phenyl carbinol (1-phenyl-3-buten-1-ol)

(2-Ethyl-1-butanol)

Ethylisobutyl carbinol (5-methyl-3-hexanol)

10.2. General Methods of Preparation. 1. The hydration of olefins in the acid medium. This method is of great industrial importance, because it allows us to obtain alcohols from gases of petroleum cracking. Primary alcohol, or ethanol, is obtained from ethylene, while only secondary and tertiary alcohols are obtained from other olefins. Addition occurs according to Markovnikov's rule:



The method of *direct hydration* is used industrially, it is carried out by passing a mixture of olefin and water vapour over a phosphate catalyst (see Sec. 4.5).

2. Another important industrial method is the fermentation of carbohydrates (see Sec. 10.5), in which primary pentyl (amyl) alcohols, propyl alcohol and primary butyl alcohols (*n*- and *iso*-) are obtained together with the principal product: ethyl alcohol.

3. Hydrolysis of the halogen derivatives:

$$RX + HOH \rightarrow ROH + HX$$

This reaction was considered in detail in Sec. 9.4.

The method is important in obtaining alcohols from hydrocarbons. When a mixture of isomeric chloropentanes (which are obtained by chlorinating isopentane) is being hydrolyzed, a mixture of isomeric pentyl alcohols is formed, and the highest-boiling 1-pentanol can be isolated from these alcohols by distillation. A mixture of pentyl alcohols is used as a solvent.

4. Reduction of carbonyl compounds. The reduction of aldehydes causes the formation of primary alcohols, while the reduction of ketones, the formation of secondary alcohols:

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + 2H \rightarrow \underset{\text{Ethyl alcohol}}{CH_3-CH_2OH}$$

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 2H \rightarrow \underset{\text{Isopropyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$$

There are also other important syntheses of alcohols: from aldehydes and ketones with the aid of organomagnesium compounds and from primary amines under the action of nitrous acid. These methods will be dealt with later.

10.3. Physical Properties. Association. Hydrogen Bonding. Physical properties. The lower and middle members of the series of saturated monohydric alcohols (C_1-C_{11}) are liquids whose boiling points rise as the composition becomes more complex. Higher alcohols from C_{12} are solids. Alcohols having an *iso* structure boil at a lower temperature than those having a normal structure. The lower representatives have a characteristic alcoholic odour and a burning taste, the middle representatives, C_4-C_6, an unpleasant odour, and the higher ones are odourless. The density of alcohols is less than unity, and only that of some aromatic alcohols is higher than unity. The first three members of the saturated alcohol series mix with water in all proportions, but solubility diminishes as the radical becomes more com-

plex. Higher alcohols, like hydrocarbons, are practically water-insoluble. Table 10.1 gives the properties of some alcohols.

TABLE 10.1. **Physical Properties of Some Alcohols**

Names of alcohols	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Methanol	CH_3OH	—98	64.7	0.79
Ethanol	$CH_3—CH_2OH$	—117	78.3	0.79
Propanol	$CH_3—CH_2—CH_2OH$	—127	97.2	0.80
Isopropanol	$CH_3—CH(OH)—CH_3$	—88.5	82.2	0.78
Allyl alcohol	$CH_2=CH—CH_2OH$		96.7	0.85
Decanol	$CH_3—(CH_2)_8—CH_2OH$	6	228	0.80
Cyclohexanol	$C_6H_{11}OH$	25.5	161.5	0.96
Benzyl alcohol	$C_6H_5—CH_2OH$	—	205	1.04
β-Phenyl ethanol	$C_6H_5—CH_2—CH_2OH$	—	220	1.02

The boiling point of alcohols is higher than that of other compounds having a similar molecular mass:

	Molecular mass	Boiling point, °C
$CH_3—CH_3$	30	—88.6
CH_3Cl	50.5	—24.2
CH_3NH_2	31	—6.7
CH_3SH	48	+7.6
CH_3OH	32	+64.7

This shows the similarity between alcohols and water, whose boiling point is considerably higher than it should be by its molecular mass (an analogue of water, hydrogen sulphide H_2S, boils at —60°C).

Association of Alcohols. Hydrogen Bonding. The molecules of alcohols in solid and liquid states, like water molecules, are *associated*; in this case, the molecular mass of a substance considerably increases and, consequently, its volatility decreases. Association is interrupted as alcohols pass over to a vapour state. Association is said to be caused by hydrogen bonds which originate between molecules.

The hydrogen bond is a special type of bond which originates at the expense of the hydrogen atom of such functional groups as —OH, —COOH and $—NH_2$, and of electronegative atoms (O, N, F, etc.) which possess free electron pairs. There is electrostatic interaction between the partially positively charged hydrogen (one functional group) and the partially negatively charged atom X (another functional group). The higher the fractional positive charge

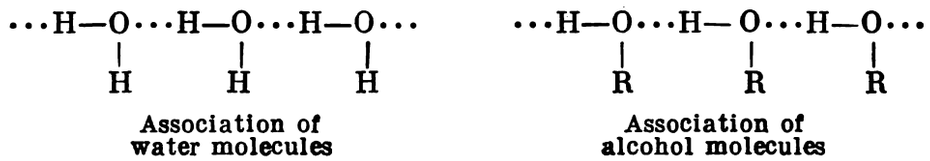
of the hydrogen atom, the more readily is the hydrogen bond formed (this bond is usually denoted by three dots):

$$\cdots H{-}X\cdots H{-}X\cdots H{-}X\cdots$$

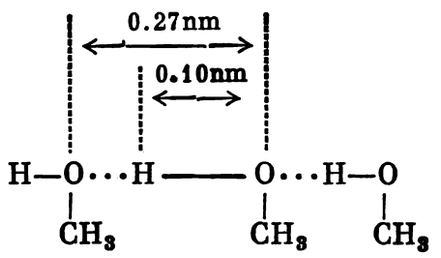
Besides electronegativity, the atomic size is important in the formation of the hydrogen bond. For example, nitrogen and chlorine have similar electronegativity (ca. 3), but the small size of the nitrogen atom and the higher concentration of its charge allow it to approach the hydrogen nucleus closer than the chlorine atom, whose radius is greater than that of the nitrogen atom. Therefore, chlorine tends to form the hydrogen bond less than nitrogen.

Hydrogen atoms do not form the hydrogen bond in nonpolar molecules and hydrocarbon radicals.

In the hydroxyl group, the oxygen-hydrogen covalent bond is polarized, and this causes intermolecular interaction between hydrogen, which bears a partial positive charge, and oxygen, which bears a partial negative charge:



The energy of formation of the hydrogen bond is usually not higher than 20-30 kJ/mole, while the average energy of the covalent bond varies in the range of 335-460 kJ/mole. The distance between two oxygen atoms in two associated alcohol (or water) molecules is 0.27 nm, while the average distance between molecules of nonassociated substances in a liquid state is 0.34 nm. The hydrogen atom is closer to one of the oxygen atoms with which it is linked by a covalent bond:



When alcohols dissolve in water, they form new hydrogen bonds with water molecules.

The less branched is the carbon chain of alcohol and the smaller is the number of alkyl groups that surround the carbon atom to which the hydroxyl is attached, the more readily does association occur, and therefore primary alcohols and alcohols of a normal structure

have higher boiling points. For example, butyl alcohols C_4H_9OH have the following boiling points:

	Boiling point, °C		Boiling point, °C
n-Butanol	117.7	*sec*-Butanol	99.5
Isobutanol	107.3	*tert*-Butanol	82.8

When the hydrogen atom of the hydroxyl group in alcohols is replaced by other atoms (or groups), the hydrogen bond disappears and this immediately affects the boiling point:

CH_3CH_2OH	CH_3CH_2Cl	$CH_3CH_2—O—CH_2CH_3$
78.3°C	13°C	34.6°C

The foregoing examples of the hydrogen bond relate to intermolecular bonds. The hydrogen bond can originate also inside the same molecule.

Strong hydrogen bonds are formed by carboxylic acids (see Sec. 12.3). Signs of weak hydrogen bonds due to insufficient polarity of the H—C bond have been detected in chloroform $H—CCl_3$ and hydrocyanic acid H—C≡N.

Hydrogen bonds are of great significance in such biologically important natural substances as proteins, enzymes and cellulose, and also in synthetic polyamides.

10.4. Chemical Properties. The functional group of alcohols, the hydroxyl, determines the main chemical properties of these compounds. Alcohols are characterized by great chemical activity. Owing to the diversity of reactions which alcohols undergo and the availability of raw material for obtaining them, alcohols are valuable starting material for synthesizing many aliphatic compounds.

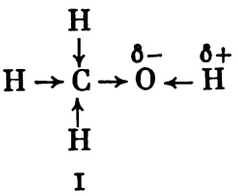
The carbon-oxygen and oxygen-hydrogen C—O—H bonds are polarized, and oxygen, being the most electronegative element, constitutes the negative end of the dipole. Carbon and hydrogen atoms bear partial positive charges.

Such an electronic nature of the hydroxyl group predetermines its tendency to undergo reactions of the heterolytic type, in which either the C—O bond or the O—H bond can be ruptured.

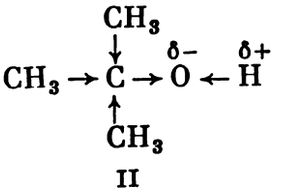
Acid and basic properties. Formation of alkoxides. Alcohols are practically neutral substances: they do not change the colour of indicators and do not react with either aqueous solutions of alkalies or dilute acids. However, in certain reactions, alcohols exhibit properties of very weak acids and bases, i.e., they are amphoteric, like water.

The *acid properties* of alcohols are expressed more weakly than those of water, although the oxygen-hydrogen bond is polarized: $\overset{\delta-}{O}—\overset{\delta+}{H}$. Alkyl groups repel electrons (I), and therefore the proton is eliminated less readily in comparison with water. The acid pro-

perties of tertiary alcohols are expressed the most weakly, as is exemplified by trimethylcarbinol II:

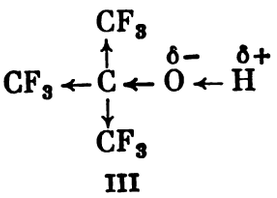


I



II

Acid properties are intensified if an electron-acceptor atom is introduced into the alcohol radical. An example is the perfluoro-derivative of trimethylcarbinol (III), whose acid properties are clearly pronounced (it decomposes carbonates):



III

The effect of methyl groups and fluorine atoms on the acidity of hydroxyl hydrogen is an example of the *inductive effect* (see Sec. 9.7).

When alkali metals act on alcohols in an anhydrous medium, hydroxyl hydrogen is forced out and *alkoxides* (or *alcoholates*) are formed:

$$2C_2H_5OH + 2Na \rightarrow \underset{\substack{\text{Sodium}\\ \text{ethoxide}\\ \text{(sodium}\\ \text{ethylate)}}}{2C_2H_5ONa} + H_2$$

The reaction of alkali metals with alcohols occurs more slowly than that with water.

Under the appropriate conditions, alcohols can form also alkoxides of other metals (Ca, Mg, Al).

Alkoxides have the nature of *salts* of a very weak acid (alcohol) with a base. They are hydrolyzed in the presence of water:

$$C_2H_5ONa + H_2O \rightarrow C_2H_5OH + NaOH$$

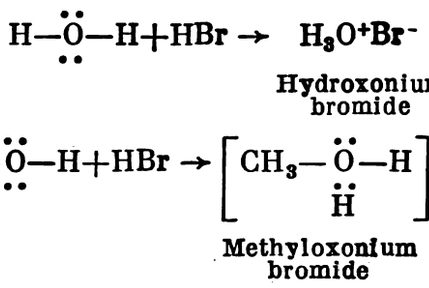
Molecules of alkoxides of alkali metals have an ionic nature: the cation is an alkali metal, while the anion, the alkoxy group R—O⁻ (alkoxide ion):

CH_3O^-	$C_2H_5O^-$	$(CH_3)_2CHO^-$	$(CH_3)_3CO^-$
Methoxide-	Ethoxide-	Isopropoxide-	*tert*-Butoxide

Alcoholic solutions of alkoxides possess strongly basic properties, and therefore they are often used in reactions for producing a strongly basic medium.

The *basic properties* of alcohols are exhibited in their interaction with strong acids. In this case, alcohols, like water, yield oxonium

salts:



Formation of ethers. *Ethers* R—O—R′ are obtained when alkoxides (or alkoxide ions, to be more exact) react with alkyl halides:

$$R—O—Na+R'I \rightarrow R—O—R'+NaI$$

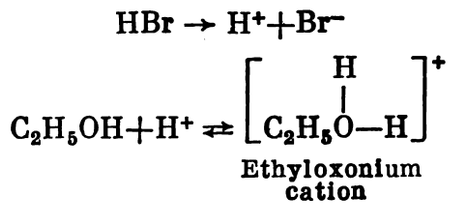
This is one of the most important methods of obtaining ethers and is a typical nucleophilic substitution reaction for halogen derivatives. Ethers are dealt with at greater length in Sec. 10.13.

Replacement of the hydroxyl group by a halogen. The action of hydrogen halides on alcohols is an important nucleophilic substitution reaction:

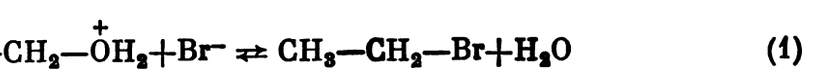
$$ROH+HBr \rightleftarrows RBr+H_2O$$

The reaction is reversible: when water acts on alkyl halides, hydrolysis occurs with the formation of alcohol. What should the conditions be for shifting the reaction to the right, i.e., towards the formation of the halogen derivative?

As we have already seen, when alcohol and a strong acid interact, the alkyloxonium ion is formed, and the water molecule readily leaves it (reactions 1 and 2). Thus, what the mineral acid does is to transfer the proton to the oxygen atom of alcohol, as a result of which the hydroxyl group is eliminated more readily:



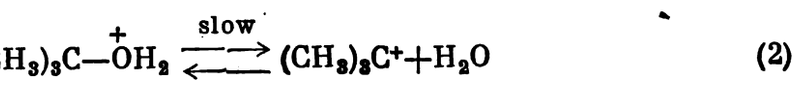
The reaction then occurs as ordinary nucleophilic substitution according to the S_N2 mechanism (this is mainly how primary alcohols react):



(1)

or according to S_N1 mechanism (tertiary alcohols):

first step



(2)

second step

$$(CH_3)_3C^+ + Br^- \xrightarrow{\text{fast}} (CH_3)_3C{-}Br$$

Formation of esters (esterification). Alcohols are characterized by a reaction with acids that results in the formation of esters. This reaction is known as the *esterification reaction.* It is reversible, because esters are hydrolyzed under the action of water which is the by-product when esters are being formed.

Esters of Mineral Acids. Both acidic and neutral esters of sulphuric acid are formed when concentrated sulphuric acid acts on alcohols. *Acid alkyl sulphates* or *alkyl sulphuric acids* are obtained when H_2SO_4 acts on alcohol (the reaction mechanism is similar to that when alkyl halides are being obtained):

$$CH_3CH_2OH + HOSO_3H \rightleftarrows [CH_3CH_2{-}\overset{+}{O}H_2 + {}^-OSO_3H] \rightleftarrows \underset{\text{Ethylsulphuric acid}}{CH_3CH_2{-}OSO_3H} + H_2O$$

Neutral esters can be prepared in various ways. For example, the action of sulphuric anhydride on methanol gives dimethyl sulphate:

$$2CH_3OH + 2SO_3 \rightarrow (CH_3O)_2SO_2 + H_2O$$

Dimethyl sulphate is an important reagent for carrying out methylation reactions, e.g., it is used for obtaining methyl ethers (see Sec. 10.13).

When concentrated nitric acid acts on alcohols, its esters, *nitrates,* are obtained:

$$C_2H_5OH + HONO_2 \rightleftarrows \underset{\substack{\text{Ethyl}\\\text{nitrate}}}{C_2H_5ONO_2} + H_2O$$

It is very difficult to practically carry out this reaction owing to the oxidizing action of nitric acid. The nitrates are explosive.

Esters of Carboxylic Acids. Alcohols and carboxylic acids interact more readily when a small amount of mineral acid is present (for details, see Sec. 12.19):

$$CH_3{-}C\begin{matrix}\diagup\!\!\!=O\\\diagdown OH\end{matrix} + HOC_2H_5 \rightleftarrows \underset{\text{Ethyl acetate}}{CH_3{-}C\begin{matrix}\diagup\!\!\!=O\\\diagdown OC_2H_5\end{matrix}} + H_2O$$

Dehydration of alcohols. Alcohols are capable of losing water under definite conditions. Concentrated sulphuric or phosphoric acid can be used as a dehydrating agent. Tertiary alcohols are dehydrated most readily, while primary ones, with greater difficulty. This is

illustrated by the conditions of dehydration of butyl alcohols:

n-Butyl alcohol	75-percent H_2SO_4, 170°C
sec-Butyl alcohol	60-percent H_2SO_4, 100°C
tert-Butyl alcohol	20-percent H_2SO_4, 90°C

Alcohols dehydrate also when their vapours are passed over a heated solid catalyst (silica gel, kaolin, aluminium oxide, thorium oxide, etc.).

The reaction can occur in one of the following ways, depending on the conditions: under severe conditions (when the temperature is higher), each alcohol molecule loses a water molecule and olefin is formed (*intramolecular dehydration*), and under mild conditions (when the temperature is lower), the water molecule is eliminated from two alcohol molecules and ethers are formed (*intermolecular dehydration*):

$$CH_2{=}CH_2 \xleftarrow[\text{or } H_2SO_4;\ 170\,^\circ C]{Al_2O_3;\ 350\,^\circ C} CH_3{-}CH_2OH \xrightarrow[\text{or } H_2SO_4;\ 140\,^\circ C]{Al_2O_3;\ 250\,^\circ C} (CH_3CH_2)_2O$$

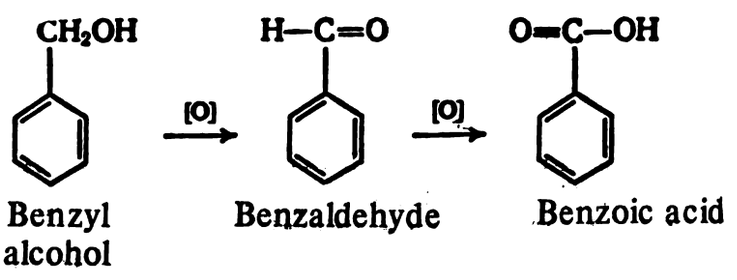
Ethylene — Ethyl ether

Oxidation of alcohols. Alcohols are oxidized more readily than hydrocarbons, and the first to be oxidized is the carbon to which the hydroxyl group is attached. Primary and secondary alcohols are oxidized more readily than tertiary ones owing to the presence of hydrogen at the carbon atom which is linked with the hydroxyl.

Different products can be formed, depending on the nature of alcohol and the reaction conditions. For example, *primary alcohols* yield at first aldehydes, and then acids having the same number of carbon atoms:

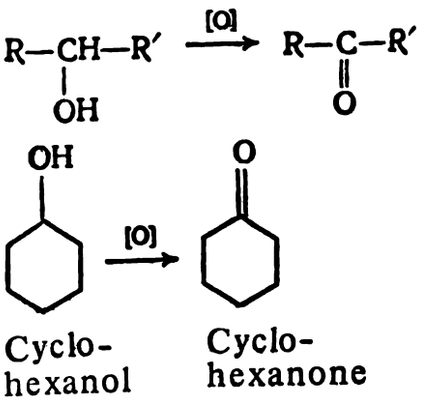
$$CH_3{-}CH_2{-}CH_2OH \xrightarrow{[O]} CH_3{-}CH_2{-}C{\overset{O}{\diagdown\!\!\diagup}}H \xrightarrow{[O]} CH_3{-}CH_2{-}C{\overset{O}{\diagdown\!\!\diagup}}OH$$

Propyl alcohol — Propanal — Propionic acid



Benzyl alcohol — Benzaldehyde — Benzoic acid

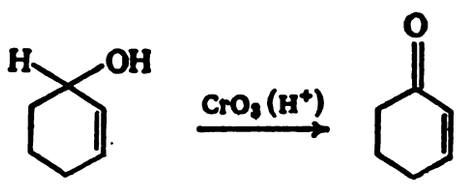
Ketones are formed from *secondary alcohols*:



Cyclo-hexanol Cyclo-hexanone

Tertiary alcohols are more stable towards oxidation, but under the action of strong oxidizing agents, the carbon-carbon bond can be cleaved, and ketones and acids of lower carbon content than initial alcohol can be formed.

The chromic-acid mixture is the most suitable oxidizing agent of primary and secondary alcohols up to aldehydes and ketones in the laboratory. It can be used also for oxidizing unsaturated alcohols with the preservation of the double bond, because it acts slowly on the multiple bond:



2-Cyclohexen-1-ol 2-Cyclohexen-1-one

When alcohols burn up, they form carbon dioxide and water:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$$

Catalytic dehydrogenation of alcohols. Alcohols can be converted into aldehydes and ketones also by dehydrogenation, i.e., by passing alcohol vapours over a heated metallic catalyst, such as copper or silver at 300°C, without adding an oxidizing agent. A typical dehydrogenation reaction is the conversion of ethyl alcohol into acetaldehyde:

$$CH_3—CH_2OH \xrightarrow{Cu;\ 300\ ^\circ C} CH_3—C\overset{O}{\underset{H}{<}} + H_2$$

This reaction is endothermic. The best temperature can be maintained by burning a part of hydrogen being evolved. In industry, the principle of continuous flow is applied, using an inexpensive

oxidizing agent, i.e., air (this should be done under stringent control so as to preclude deeper oxidation):

$$CH_3—OH \xrightarrow[\text{catalyst}]{1/2O_2;} H—C\overset{O}{\underset{H}{<}} + H_2O$$

Formaldehyde

Oxygen acts as an acceptor for hydrogen which is eliminated under catalytic action.

Chugaev-Tserevitinov reaction. This reaction is the basis of the analytical method of determining *active hydrogen* (hydrogen of the hydroxyl group) in alcohols. Alcohols and methylmagnesium iodide interact by the following equation:

$$R—OH + CH_3MgI \rightarrow R—OMgI + CH_4$$

The number of hydroxyl groups in the alcohol molecule can be determined when the weighed portion of the test substance is known and the amount of methane evolved is measured.

10.5. Important Individual Monohydric Alcohols. *Methyl alcohol (methanol)* is obtained industrially in large amounts by the following methods:

1. Synthesis from carbon monoxide and hydrogen. The catalysts of this reaction are chromium and zinc oxides, the temperature is 350°C, and pressure, 250 kg/cm²:

$$CO + 2H_2 \rightarrow CH_3OH$$

2. Partial oxidation of methane in the presence of compounds of copper and manganese as catalysts:

$$CH_4 + {}^1/_2O_2 \rightarrow CH_3OH$$

This method requires stringent technological control, because the alcohol being formed can be oxidized further into formaldehyde and formic acid. Methyl alcohol is obtained as the principal product when pressure is high, methane is in excess and a mixture of gases is passed through rapidly.

3. Methyl alcohol is also obtained as a by-product in the dry distillation of wood (and hence its old name "wood" alcohol). At present, this method is used only in processing wood wastes.

In industry, methyl alcohol is used mainly for obtaining formaldehyde. It is employed also for synthesizing methylating agents (methyl chloride, dimethyl sulphate), dimethylaniline, and for obtaining acetic acid (see Sec. 12.5). Methyl alcohol is a solvent of organic substances. It is toxic in any doses, causing blindness in small doses, and death in large ones.

Ethyl alcohol (ethanol) has a peculiar alcoholic odour and a burning taste. Ordinary alcohol contains about 4.5 per cent of water. This

azeotropic mixture, which is distilled off inseparably, boils at 78.15°C (760 mm Hg).

To obtain absolute (anhydrous) alcohol, water can be removed chemically by boiling alcohol with calcium oxide or anhydrous copper sulphate. To produce absolute alcohol industrially, benzene is added to rectified spirit and the mixture is subjected to distillation. At first, the ternary azeotropic mixture, alcohol-water-benzene (b.p. 64.9°C), is distilled off. In this case, water is removed completely. Then, benzene is removed completely as a binary azeotropic mixture, alcohol-benzene, at 68.3°C, and afterwards pure alcohol is distilled off at 78.3°C.

Absolute alcohol mixes with gasoline in all proportions (unlike the 95-percent one), and therefore it can be used as fuel for internal-combustion engines. Alcohol is a good solvent of many organic substances, it possesses antiseptic properties and preserves protein.

Ethanol is obtained industrially either by synthesis or from natural complex carbohydrates (starch, cellulose).

At present, the most important synthetic methods are ethylene hydration (see Sec. 4.5) and the catalytic reduction of acetaldehyde obtained by Kucherov's reaction (see Sec. 5.4).

In the oldest method of alcohol production, the alcoholic fermentation of saccharides, carbohydrates (the most important of which is glucose $C_6H_{12}O_6$) are subjected to splitting (fermentation) in the presence of special microorganisms: yeasts. The mechanism of the fermentation reaction is complicated and, on the whole, the fermentation process can be expressed by the following equation:

$$C_6H_{12}O_6 \rightarrow 2CO_2+2C_2H_5OH$$

The raw material used can be berries, grapes and beet syrup, which contain saccharides in a free state (this is how grape, fruit and berry wines are obtained), and also starch-containing substances: grain, maize and potatoes. Starch $(C_6H_{10}O_5)_x$ is subjected at first to "saccharification", i.e., to hydrolysis up to glucose, and then to fermentation.

To obtain alcohol for technical purposes, a polysaccharide, cellulose, is also used in industry. To this end, the wastes of the woodworking industry (sawdust, chips, etc.) are hydrolyzed by 5-percent sulphuric acid under a pressure of 10 kg/cm^2. Hydrolyzates contain mainly glucose. The hydrolyzate is neutralized by lime (sulphuric acid precipitates as $CaSO_4$), and then it is passed through a filter and fermented (*hydrolysis alcohol* is obtained):

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_x} \xrightarrow{\text{hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{fermentation}} \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

One ton of sawdust yields the same amount of alcohol as one ton of potatoes or 300 kg of grain.

Ethyl alcohol is among the most important industrial products. About 80 per cent of the alcohol being produced is used for industrial purposes and for manufacturing synthetic rubber by Lebedev's method (Sec. 6.3). Synthetic rubber is now being increasingly produced from crude oil.

Alcohol is employed as a solvent for extraction and crystallization, for making lacquers and paints, preserving anatomical preparations, preparing medicinals, and producing eau de Cologne and perfume in perfumery, and as a disinfectant in medicine. A large amount of alcohol is used for synthesizing ether, ethyl chloride, esters of organic acids, chloroform, iodoform, etc. It was already noted earlier that alcohol can be employed also as motor fuel.

Alcohol intended for technological processes is denatured: it is made unfit for drinking by adding methyl alcohol, formalin or pyridine to it. Such alcohol is poisonous.

Propyl, butyl and amyl alcohols are used in their free state and in the form of acetic esters as solvents. Butyl esters of dibasic and higher monobasic acids are used as plasticizers. The oil-refining industry supplies raw material for obtaining these alcohols.

Higher Fatty Alcohols (HFA). At the beginning of the nineteenth century, the French chemist Chevreul was the first to isolate higher fatty alcohol $C_{16}H_{33}OH$ from a fatty substance found in the head of the sperm whale, and he called it *cetyl alcohol* (from the Latin word "cetus", meaning "whale"). This substance is similar to fat by its appearance, and its melting point is 50°C. There are the following types of alcohol, depending on the length of the radical and on consistency: (1) C_6-C_{12}, syrup-like liquids whose b.p. is 157-263°C; (2) C_{13}-C_{20}, grease-like substances which have the appearance of solidified lard; their m.p. is 31-66°C and they are more similar to hydrocarbons by their properties, and (3) C_{21}-C_{40} are solids whose m.p. is 69-95°C.

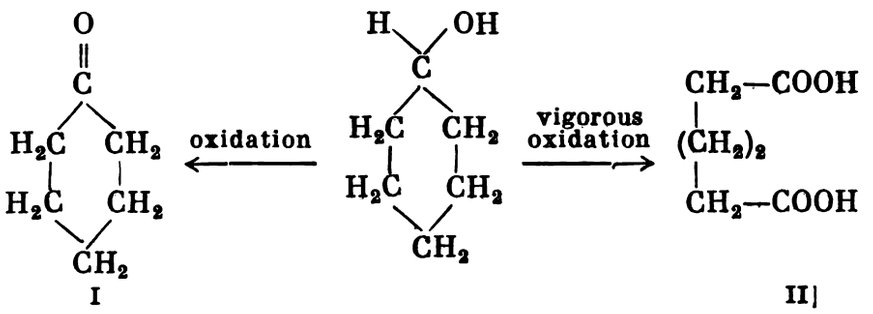
Until the end of the 1940's, the main source of HFA was whale fat. At present, HFA is produced synthetically in a large amount. About one million tons of these alcohols are being produced in the world annually. The oil-refining industry supplies the raw material for obtaining them. One of the syntheses is the reduction of higher fatty acids obtained by paraffin oxidation. Secondary HFA can be prepared by directly oxidizing normal paraffins by oxygen in the presence of boric acid. Primary normal alcohols C_6-C_{20} are obtained by polymerizing ethylene by Ziegler's method with subsequent oxidation and hydrolysis (see Sec. 17.3).

Higher fatty alcohols are used as surfactants: anti-evaporation agents (for protecting reservoirs), frothing agents (ore flotation), etc. They are good solvents. Diesters on the basis of HFA are good plasticizers, and they are employed as lubricants for aircraft engines operating in the —50-+200°C range. Higher fatty alcohols are used

in a large amount for obtaining synthetic detergents, whose advantage is that they are completely destroyed when waste waters are biochemically purified, and therefore they do not contaminate reservoirs. These alcohols are the basis for obtaining quaternary ammonium salts, whose addition in microscopic amounts to water sterilizes it, and this is of great importance in the food industry when meat, fish, fruits and vegetables are being processed, apparatus is being washed, and so forth.

Cyclohexanol, $C_6H_{11}OH$, is, at room temperature, a crystalline substance (m.p. 25.5°C) having a characteristic camphoric odour. It is manufactured industrially by hydrogenating phenol (Sec. 10.9).

When cyclohexanol is being oxidized, ketone cyclohexanone I or adipic acid II is obtained, depending on the conditions, and they are used industrially for producing the synthetic fibres called capron and nylon (see Secs. 11.5 and 23.7):



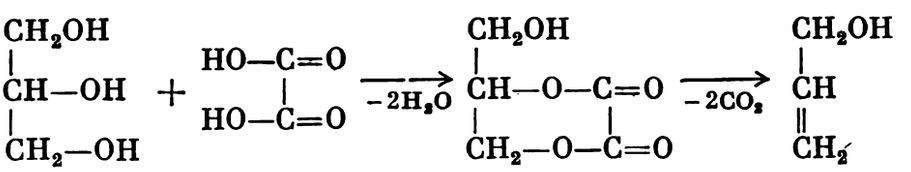
I II

Allyl alcohol, $CH_2=CH-CH_2OH$, is a representative of unsaturated alcohols. It is obtained industrially from propylene by high-temperature chlorination and subsequent hydrolysis:

$$CH_2=CH-CH_3 \xrightarrow{Cl_2;\ 500\,^\circ C} CH_2=CH-CH_2Cl \xrightarrow{HOH} CH_2=CH-CH_2OH$$

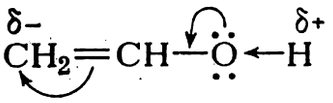
Allyl alcohol is an intermediate product in glycerol synthesis (see Sec. 10.6).

Conversely, allyl alcohol is obtained in the laboratory by heating glycerol with oxalic acid:



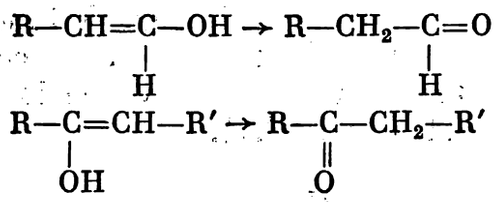
Unsaturated alcohols which are of the type of vinyl alcohol $CH_2=CHOH$ and which contain the hydroxyl group at the carbon atom that is linked by a double bond, known as *enols*, are unstable in the free state (Eltekov-Erlenmeyer rule). Vinyl alcohol is unstable, because the free electron pairs of oxygen become conjugated with

the π-electrons of the double bond:



As the hydrogen atom of the hydroxyl group becomes highly positively charged, it readily removes as a proton, which is added to the carbon atom of the CH_2 group that has excess electron density.

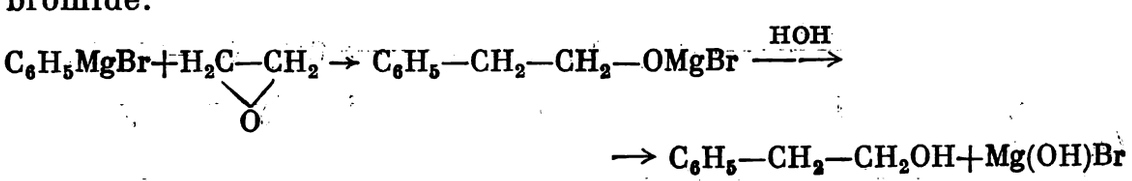
When such alcohols are being formed, they isomerize into carbonyl compounds, i.e., into aldehydes and ketones:



Ethers and esters of these alcohols are stable. They are used industrially. Ethers are obtained when alcohols react with acetylene (see Sec. 10.13), and esters, when carboxylic acids react with acetylene (see Sec. 12.19).

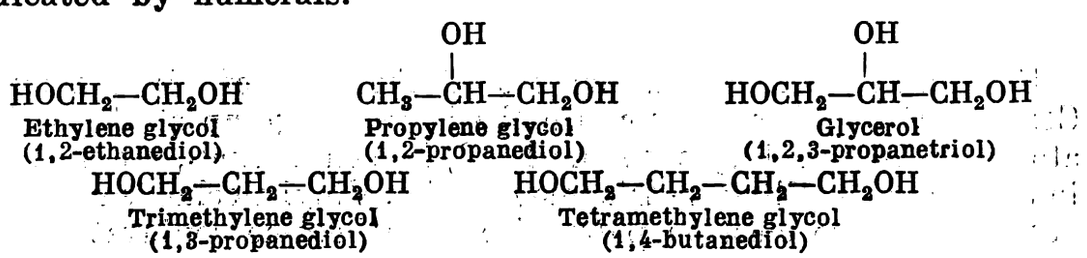
Benzyl alcohol, $C_6H_5—CH_2OH$, is the simplest aromatic alcohol, and it is found in the free state and as esters in the essential oils of jasmine and other flowers. It is used in perfumery. It is obtained by hydrolyzing benzyl chloride and also by reducing benzaldehyde.

β-Phenyl ethyl alcohol, $C_6H_5—CH_2—CH_2OH$, is the main component of rose oil. It is used in perfumery. In industry, it is synthesized by the reaction between ethylene oxide and phenyl magnesium bromide:



POLYHYDRIC ALCOHOLS

10.6. Nomenclature. Physical Properties. Individual Representatives. Dihydric alcohols are known as *glycols* or *diols*, and trihydric ones, as *glycerols* or *triols*. The position of the hydroxyl groups is indicated by numerals:



Polyhydric alcohols dissolve well in water and poorly in organic solvents, and they have high boiling points (owing to molecular association).

Glycols can be prepared by methods similar to those used for obtaining monohydric alcohols.

Ehylene glycol. The most important diol is ethylene glycol. It is a colourless liquid whose b.p. is 197°C, and d_4^{20}, 1.11, it mixes with water in all proportions. It is produced industrially from ethylene in various ways:

$$CH_2=CH_2 \xrightarrow{O_2;\ H_2O} HOCH_2—CH_2OH$$

$$CH_2=CH_2 \xrightarrow{Cl_2} CH_2Cl—CH_2Cl \xrightarrow{H_2O} HOCH_2—CH_2OH$$

$$CH_2Cl—CH_2OH \xleftarrow{HClO} CH_2=CH_2 \xrightarrow{O_2(Ag)} H_2C—CH_2$$

$$CH_2Cl—CH_2OH \xrightarrow{H_2O} HOCH_2—CH_2OH \xleftarrow{H_2O} H_2C—CH_2 \quad (O)$$

The chemical properties of ethylene glycol and of polyhydric alcohols in general are similar to those of monohydric alcohols. Two series of derivatives are obtained, depending on whether one or both hydroxyl groups participate in a reaction.

Glycols, like monohydric alcohols, do not change the colour of indicators, but ethylene glycol is somewhat more acidic than ethyl alcohol. Acidity intensifies as the number of hydroxyl groups increases. *Glycolates* are formed under the action of not only alkali metals, but also hydroxides of heavy metals. For example, copper glycolate (dark blue) is obtained when ethylene glycol reacts with freshly precipitated cupric hydroxide. Glycolates of heavy metals are readily formed not only because of the higher acidity of ethylene glycol, but also because of the higher stability of these glycolates, which have the nature of chelate compounds:

$$2\begin{matrix}CH_2—OH\\|\\CH_2—OH\end{matrix} + Cu(OH_2) \rightarrow \begin{matrix}CH_2—O\\|\\CH_2—O\end{matrix}\!\!>\!Cu\!<\!\!\begin{matrix}O—CH_2\\|\\O—CH_2\end{matrix} + 2H_2O$$

(H above the O—CH$_2$ group; H below the CH$_2$—O group)

Hydroxyl groups in ethylene glycol can be replaced by a halogen. One hydroxyl group is replaced under the action of hydrogen chloride or hydrogen bromide, and halohydrin is obtained:

$$\begin{matrix}CH_2—OH\\|\\CH_2—OH\end{matrix} \xrightarrow{HCl} \begin{matrix}CH_2—Cl\\|\\CH_2—OH\end{matrix}$$

Glycol — Ethylene chlorohydrin

The second hydroxyl is replaced with greater difficulty, and more readily by the action of PCl_5 or $SOCl_2$.

Ethylene glycol forms ethers and esters. Some of them are used industrially; for example, methyl cellosolve, $CH_3OCH_2CH_2OH$, a liquid which boils at 125°C, is employed as a solvent.

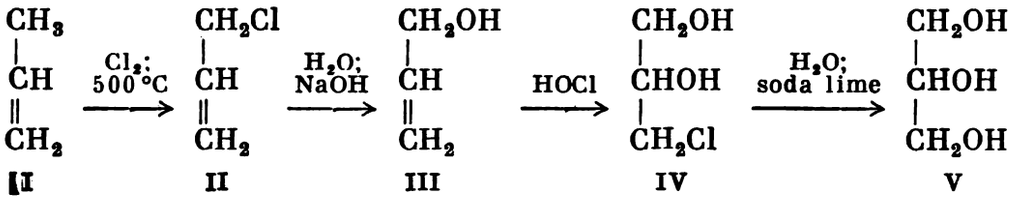
The 50-percent aqueous solution of ethylene glycol is used as an antifreeze for cooling automobile engines (it freezes at —34°C).

Glycerol (1,2,3-*propanetriol*) is the most important representative of polyhydric alcohols. Under ordinary conditions, it is a viscous hygroscopic liquid with a sweet taste (m.p. 17°C, b.p. 290°C, d_4^{20} 1.26). It mixes with water in all proportions.

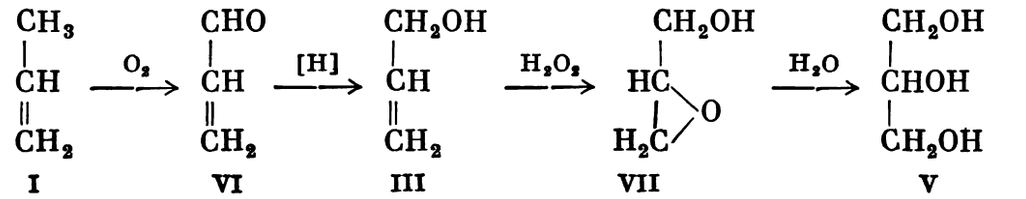
Glycerol is in combination with various fatty acids in all animal and vegetable fats and oils.

The oldest method of producing glycerol industrially is the hydrolysis of fats and oils (see Sec. 12.22). In a modern and important industrial method, use is made of propylene, which is a product of petroleum refining. Propylene can be converted into glycerol in various ways.

Allyl chloride II is obtained when propylene I is thermally chlorinated, and allyl alcohol III, when allyl chloride is hydrolyzed. Allyl alcohol is converted, under the action of hypochlorous acid ($Cl_2 + H_2O$), into 3-chloro-1,2-propanediol IV, and the latter is hydrolyzed into glycerol V:



A more promising method is the oxidation of propylene by atmospheric oxygen (catalyst Cu, 370°C) to acrolein VI, which is reduced to obtain allyl alcohol III. Allyl alcohol III is converted, under the action of hydrogen peroxide, into glycide alcohol VII (*glycidol*), while the latter is hydrolyzed into glycerol V:



Glyceraldehyde is obtained when hydrogen peroxide acts directly on acrolein, and then glyceraldehyde is converted into glycerol by catalytic hydrogenation:

$$CH_2{=}CH{-}CHO \xrightarrow{H_2O_2} CH_2OH{-}CHOH{-}CHO \xrightarrow{H_2/Ni} CH_2OH{-}CHOH{-}CH_2OH$$

Glycerol can be obtained from acetylene and formaldehyde:

$$CH{\equiv}CH + CH_2O \rightarrow \underset{\text{Propargyl alcohol}}{CH{\equiv}C{-}CH_2OH} \xrightarrow{H_2(Pd)} \underset{\text{Allyl alcohol}}{CH_2{=}CH{-}CH_2OH} \xrightarrow{H_2O_2} \underset{\text{Glycerol}}{CH_2OH{-}CHOH{-}CH_2OH}$$

The production of glycerol by hydrolyzing food fats is gradually losing its importance.

Glycerol is similar to ethylene glycol by its properties: it readily gives, with the hydroxides of heavy metals, *glycerates*; the hydroxyl groups are exchanged for a halogen, and they form ethers and esters. The ester of glycerol and nitric acid, glyceryl trinitrate, is inaccurately called "nitroglycerin":

$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} \xrightarrow[H_2SO_4]{HONO;} \begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array}$$

At room temperature, it is a shock-sensitive and highly explosive liquid (m.p. 13°C, *d* 1.6).

Nitroglycerin decomposition is a highly exothermic reaction (3000°C) in which a large amount of gases is liberated:

$$4\begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array} \rightarrow 12CO_2 + 6N_2 + 10H_2O + O_2$$

To enhance the stability of nitroglycerin and make it safer to handle, a porous mass (infusorial earth, wood meal, etc.) is impregnated with it and *dynamite* is prepared. Dynamite is used in warfare and mining.

High-molecular-weight compounds called glyptal resins (see Sec. 23.9) are formed when glycerol and dibasic phthalic acid are condensed.

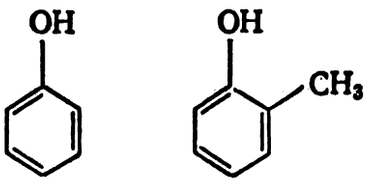
Since glycerol is hygroscopic, it is used as a moistening agent for preparing pharmaceuticals and cosmetics, and it is also employed in the tanning and textile industries. In the food industry, it is used to sweeten liqueurs, etc.

PHENOLS AND NAPHTHOLS

10.7. Phenols. Isomerism. Physical Properties. **Phenols** are hydroxyl-containing aromatic compounds in which the hydroxyl group is attached directly to a carbon atom of the benzene ring (unlike

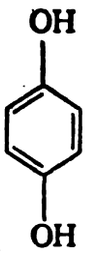
aromatic alcohols). The general formula of phenols is Ar—OH, where Ar is the aromatic radical.

There are mono-, di- and polyhydric phenols, depending on the number of hydroxyl groups:

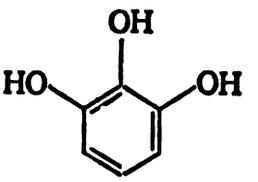


Phenol (hydroxybenzene)

o-Cresol (2-hydroxytoluene)

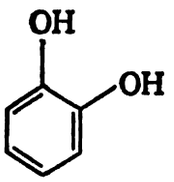


Hydroquinone (1,4-dihydroxybenzene)

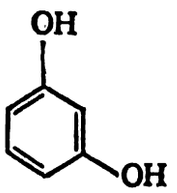


Pyrogallol (1,2,3-trihydroxybenzene)

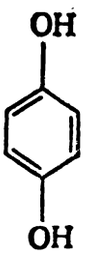
The isomerism of phenols is engendered by the position of the hydroxyl. For dihydric phenols, like for other disubstituted aromatic compounds, three isomers are known, i.e., *ortho*-, *meta*- and *para*-isomers, which have the following trivial names:



ortho-Isomer catechol or pyrocatechin (1,2-dihydroxybenzene) m.p. 105°C



meta-Isomer resorcinol (1,3-dihydroxybenzene) m.p. 110°C



para-Isomer hydroquinone (1,4-dihydroxybenzene) m.p. 171°C

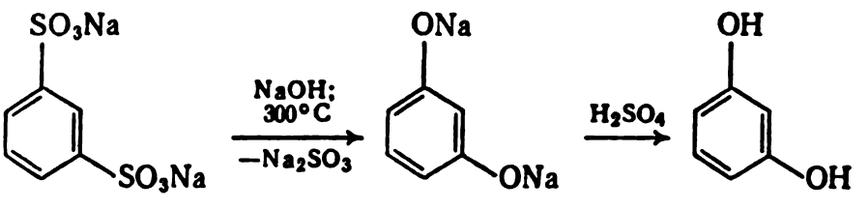
Physical properties. Phenols are crystalline substances or high-boiling liquids which have a strong characteristic odour. The density of phenols is approximately unity. Hydroxyl hydrogen is more acidic than in alcohols, and this is reflected in the physical properties of phenols. They form hydrogen bonds of greater stability, have higher boiling points and are more water-soluble than the corresponding cyclic alcohols, e.g.,

	Phenol	Cyclohexanol
Melting point, °C	41	25.5
Boiling point, °C	181	161
Water-solubility at 20°C, g/100 g	9.0	3.6

10.8. Industrial Preparations of Phenols. Large amounts of phenol and cresols (methyl phenols) are contained in the middle oil of coal tar and in wood tar. They are extracted from tar as phenoxides by treatment with a solution of sodium hydroxide, and then are precipitated by acids (see Sec. 10.9).

In the synthetic methods, the starting raw material for obtaining phenol is mainly benzene or cumene.

One of the oldest methods of obtaining phenols is of alkali fusion of sodium salts of benzenesulphonic acids. The phenoxides formed are decomposed by mineral acids. At present, the method is used mainly for obtaining polyhydric phenols:



Resorcinol
(1,3-dihydroxy-
benzene)

The most important industrial methods of obtaining the simplest phenol are Raschig's process and the cumene method.

In *Raschig's process*, the oxidizing chlorination of benzene is effected under the action of hydrogen chloride and air, and then the chlorobenzene formed is, without being isolated, hydrolyzed by water vapour in the presence of copper salts:

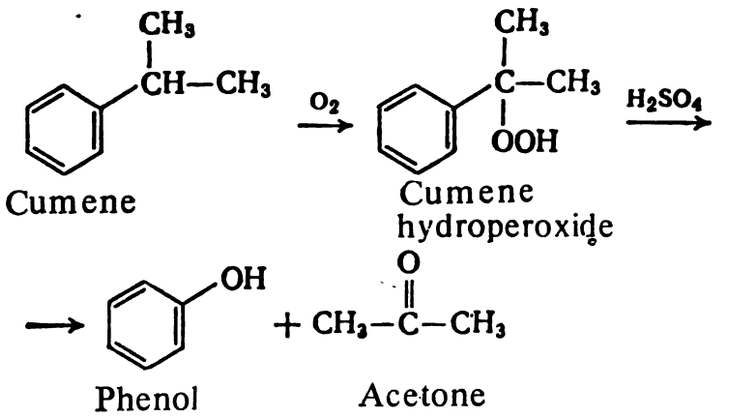
$$C_6H_6 + {}^1/_2O_2 + HCl \xrightarrow{200\ ^\circ C} C_6H_5Cl + H_2O$$

$$C_6H_5Cl \xrightarrow[\text{Cu salts}]{H_2O\ (\text{vapour});\ 500\ ^\circ C;} C_6H_5OH + HCl$$

The method is advantageous, because it does not require alkali, and hydrogen chloride is continuously regenerated.

In the *cumene method*, the initial substance is cumene (isopropylbenzene), $C_6H_5CH(CH_3)_2$, which is obtained by alkylating benzene with propylene (see Sec. 7.5). The method is economically advantageous, because another important product, acetone, is obtained together with phenol. Oxidation is effected by atmospheric oxygen, while the cumene hydroperoxide formed is decomposed by sulphuric

acid:



Cumene — Cumene hydroperoxide — Phenol — Acetone

This method was first mastered in the Soviet Union (1949). Phenols can be obtained in the laboratory by hydrolyzing diazonium salts (see Sec. 16.2).

10.9. Chemical Properties of Phenols. Phenols are similar to alcohols by their structure. But the hydroxyl group and the benzene ring which is directly attached to it strongly affect one another, and this engenders the specificity of the properties of phenols that distinguish them from aromatic alcohols.

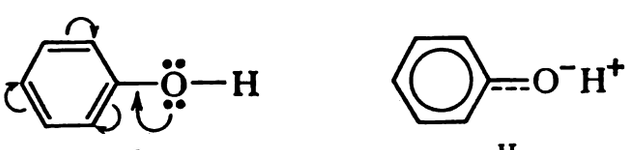
To characterize the most important properties of phenols, let us consider the reactions of the phenolic hydroxyl and of the benzene ring separately.

The *phenolic hydroxyl* is characterized by the following reactions:

1. **Acidic properties. Formation of phenoxides.** Phenols, like alcohols, do not change the colour of indicators, but their acidic properties, though being expressed weakly, are more pronounced than those of alcohols and water:

$$C_6H_5OH > H_2O > C_2H_5OH$$

Phenols are more acidic than alcohols due to the effect of the benzene nucleus. The unshared pair of electrons of the oxygen atom becomes conjugated with the π-electrons of the benzene nucleus (I). As a result, the electron density of the oxygen atom partially shifts to the oxygen-carbon bond, thus increasing the electron density in the *ortho-* and *para*-positions in the benzene nucleus. The electron pair of the oxygen-hydrogen bond is attracted more strongly to the oxygen atom, thus promoting the creation of a high positive charge on the hydrogen atom of the hydroxyl group and, consequently, the elimination of this hydrogen as a proton (II):



I II

Phenols, unlike alcohols, react with aqueous solutions of alkalies, forming *phenoxides* (therefore, the simplest phenol was called "carbolic acid", Runge, 1834).

Phenoxides, like all the salts of weak acids and strong bases, are readily hydrolyzed, and their aqueous solutions have a strongly alkaline reaction:

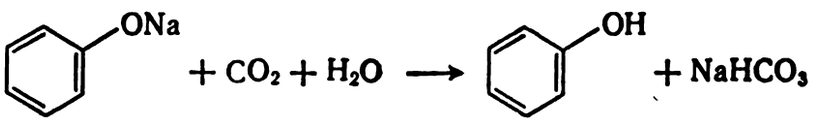
$$Ar—OH+NaOH \rightleftarrows Ar—ONa+H_2O$$

Sodium phenoxide

The hydrolysis of phenoxides occurs irreversibly under the action of strong acids:

$$C_6H_5ONa+H_2SO_4 \rightarrow C_6H_5OH+NaHSO_4$$

The acidic properties of phenols are expressed very weakly in comparison with acids. For example, phenol is considerably weaker than carbonic acid (by about 3000 times), and therefore phenols are insoluble in the aqueous solutions of carbonates of alkali metals and do not decompose carbonates. On the contrary, free phenol is formed when carbonic acid acts on phenoxide:



The phenoxide ion, $C_6H_5O^-$, is a weaker base than the alkoxide ion, because the ionic charge in it is distributed throughout the conjugated system.

The acidic properties of phenol intensify under the action of the electron-accepting groups, e.g., the nitro groups and halogens, which are linked with the ring (see Sec. 14.3).

2. **Formation of ethers.** Ethers of phenols are formed in a similar way as ethers of alcohols. Purely aromatic ethers are obtained as a result of the reaction between phenoxides and aryl halides in the presence of a catalyst, which activates a halogen in the nucleus:

$$ArONa+RX \rightarrow Ar—O—R+NaX$$

R=Alk or Ar; X=Cl, Br, I

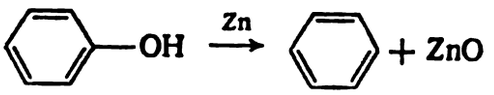
3. **Formation of esters.** Phenols, unlike alcohols, do not form esters under the direct action of acids. They are usually obtained when acid chlorides or anhydrides act on phenols:

$$C_6H_5OH+Cl-\overset{\overset{O}{\|}}{C}—CH_3 \rightarrow C_6H_5—O-\overset{\overset{O}{\|}}{C}—CH_3+HCl$$

Acetyl chloride — Phenyl acetate

4. **Replacement of the hydroxyl group by a halogen.** This reaction with phenols occurs with greater difficulty than in the case of alcohols, because the carbon-oxygen bond in phenols is stronger. Hydrohalic acids do not act on phenols. Chlorobenzene is formed with a low yield under the action of PCl_5. The process is complicated by side reactions.

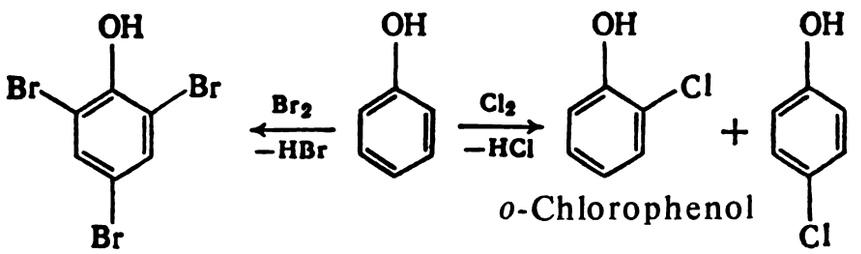
5. **Reduction.** In distillation with zinc dust, the hydroxyl group is reduced and the corresponding hydrocarbon is formed:



Reactions of the *aromatic ring*:

1. **Electrophilic substitution reactions.** The hydroxyl group is one of the strongest *ortho-para*-directing substituents (Sec. 7.6). For phenols, the electrophilic replacement of hydrogen in the benzene ring proceeds easily and under milder conditions than for benzene.

For instance, when phenols are being halogenated under the action of bromine water, three hydrogen atoms in the ring are replaced by bromine, and the tribromophenol formed falls out as a white precipitate (this is a qualitative reaction for phenols); *o*- and *p*-chlorophenols are formed when chlorine acts on phenol:

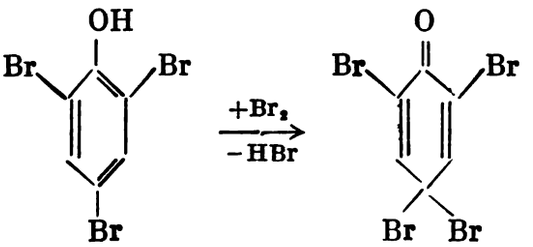


2,4,6-Tribromophenol

o-Chlorophenol

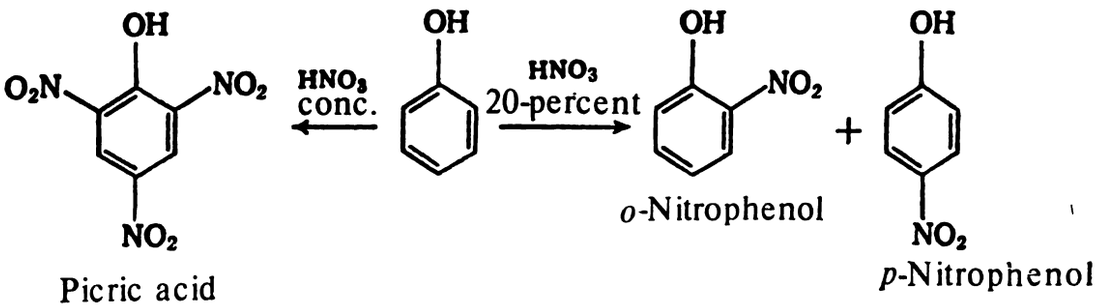
p-Chlorophenol

The reaction with bromine water usually does not end when 2,4,6-tribromophenol is formed. When the reagent is in excess, a compound of quite a different structure with four bromine atoms is formed:



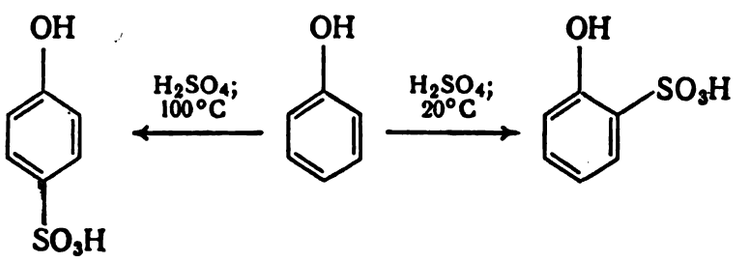
Phenol is *nitrated* under milder conditions than benzene. A mixture of *o*- and *p*-nitrophenols is formed under the action of dilute nitric

acid at room temperature; the end product of nitration is 2,4,6-trinitrophenol, which is also called *picric acid* (see Sec. 14.3):

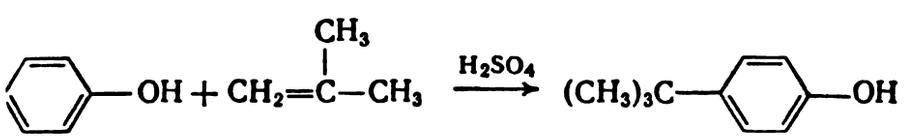


Picric acid

When phenol is *sulphonated* at room temperature, *o*-phenolsulphonic acid is produced, and at a higher temperature, the *para*-isomer is obtained:



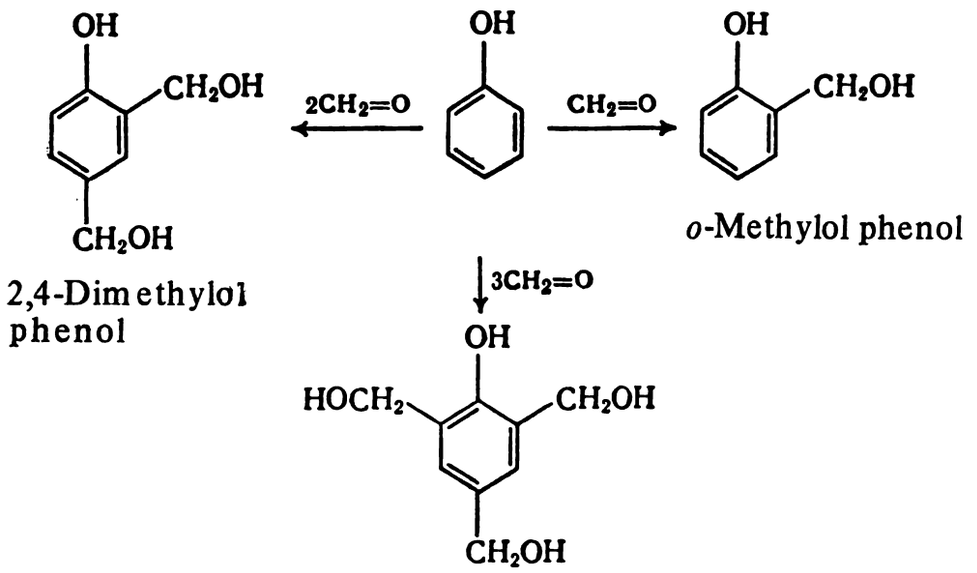
Alkylation by the Friedel-Crafts reaction, and also by alkenes and alcohols in the presence of aluminium chloride, sulphuric acid and other substances, can produce either *para*- or *ortho*-isomers, depending on the conditions. For example, the *para*-isomer is obtained in the presence of sulphuric acid:



Isobutylene 4-*tert*-Butylphenol

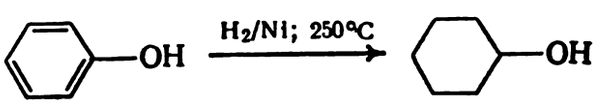
2. **Condensation reactions** with aldehydes can occur either in the acidic or alkaline medium at the expense of hydrogen atoms in *ortho*- and *para*-positions. One of the practically important reactions is the condensation of phenol with formaldehyde, in which phenolic

alcohols are formed at first:



On further condensation, phenolic alcohols produce high-molecular-weight compounds, i.e., phenol-formaldehyde resins.

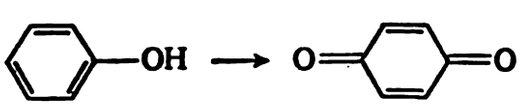
3. **Hydrogenation.** Phenols hydrogenate well in the presence of a nickel catalyst, yielding the appropriate cyclohexanols:



Cyclohexanol

The reaction is of great industrial importance (see Sec. 10.5).

4. **Oxidation of phenols.** In phenols, the presence of the hydroxyl group attached to the nucleus sharply changes the behaviour of the aromatic nucleus towards oxidizing agents. Phenols are oxidized readily, and a mixture of various oxidation products is formed. When chromic acid acts on phenol, *p*-benzoquinone can be obtained:



Phenol with ferric chloride produces a violet colour; cresols, $CH_3C_6H_4OH$, produce a dark blue colour, and polyhydric phenols,

a colour of different shades. This reaction is used for qualitatively detecting phenols.

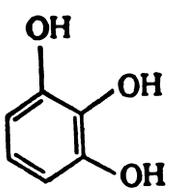
10.10. Important Individual Phenols. *Phenol* (*carbolic acid*), C_6H_5OH, is a colourless crystalline substance having a peculiar odour. It is oxidized in the air, at first becoming pink and then dark, and the crystals deliquesce as a result of hygroscopicity. It is poorly soluble in cold water, and well soluble in hot water. It mixes with alcohol, ether and benzene in all proportions. It has strongly pronounced antiseptic properties. Its aqueous solution is used for disinfection. It is toxic and causes skin burns.

Phenol is one of the most important intermediates of the modern organic synthesis industry; it is used for producing phenol-formaldehyde resins, cyclohexanol and synthetic fibres on its basis (capron, nylon); it is employed in the synthesis of dyes, medicinals, salicylic acid, herbicides, and so forth.

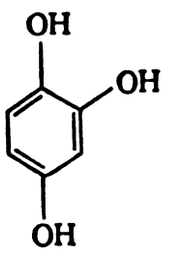
Cresols (*o-*, *m-*, *p-methyl phenols*), $CH_3C_6H_4OH$, are obtained from coal tar as a mixture called "raw cresol". It is used for producing synthetic resins and in synthesizing dyes. The aqueous emulsions of cresols with a soap solution (*Lysol*, *Creolin*) are antiseptics used in veterinary.

Di- and trihydric phenols (*dihydroxy-* and *trihydroxy-benzenes*) are crystalline substances which dissolve in water better than monohydric phenols, and they produce a colouring with ferric chloride.

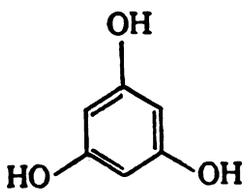
Representatives of trihydroxybenzene (dihydroxybenzenes, see Sec. 10.7) are given below:



Pyrogallol
(1,2,3-trihydroxy-benzene)
m.p. 133°C



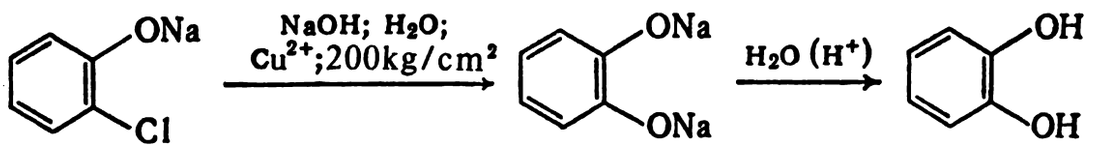
Hydroxyhydro-quinone
(1,2,4-trihydroxy-benzene)
m.p. 140°C



Phloroglucinol
(1,3,5-trihydroxy-benzene)
m.p. 219°C

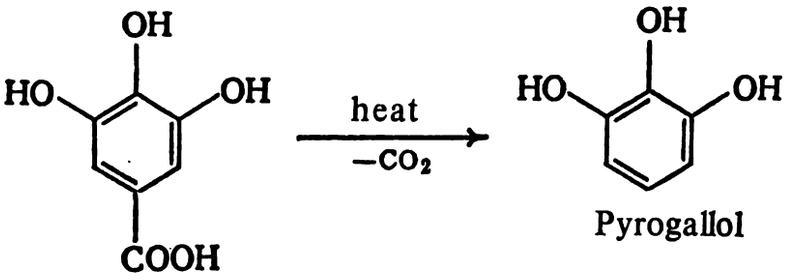
Di- and trihydric phenols are obtained industrially by subjecting sodium sulphonates to alkali fusion, a method which was described

earlier, and also by special methods, e.g.,



o-Chlorophenoxide

Pyrocatechin



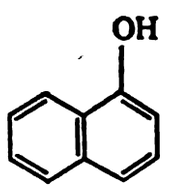
Gallic acid

Pyrogallol

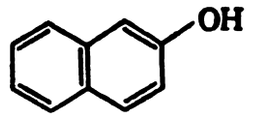
The derivatives of polyhydric phenols are found in nature as dyeing substances of plants and as tanning agents. Polyhydric phenols are used for synthesizing dyes and medicinals, for preparing polymers, etc.

When the number of hydroxyl groups in the nucleus increases, it becomes more active in electrophilic substitution reactions. The presence of several hydroxyl groups in the nucleus, especially in the *ortho-* and *para*-positions relative to one another, engenders particular sensitivity to the action of oxidizing agents. Such phenols are oxidized easily and are good reducing agents. Special mention should be made of the pronounced reducing properties of hydroquinone (1,4-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene), which are used as photographic developers. Hydroquinone is used also as an antioxidant, a substance which prevents oxidizing processes. Many alkyl phenols serve as inhibitors of polymerization in storing monomers, etc. Pyrogallol in an alkaline solution very readily absorbs molecular oxygen (from the air or other gaseous mixtures), and this is used in the analysis of gaseous mixtures for quantitatively determining oxygen.

10.11. Naphthols. Among the hydroxy derivatives of naphthalene, α- and β-naphthols are of certain interest:



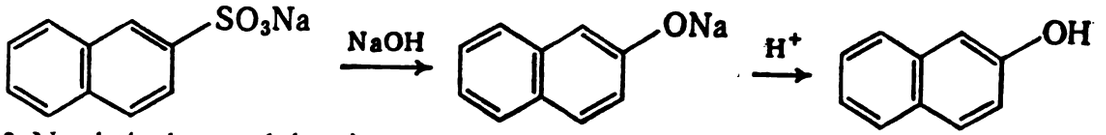
α-Naphthol
(m.p. 96°C;
b.p. 288°C)



β-Naphthol
(m.p. 122°C;
b.p. 294°C)

They possess the properties of phenols, dissolve in alkalies and produce a colouring with ferric chloride (α-naphthol produces a violet colour, and β-naphthol, green).

They are prepared industrially by subjecting sodium naphthalenesulphonates to alkali fusion:



β-Naphthalenesulphonic acid

β-Naphthol

Naphthols and their derivatives, especially sulpho derivatives, are widely used in azo dye production.

ETHERS. EPOXIDES

10.12. Nomenclature. Isomerism. Physical Properties. *Ethers* are compounds in which two hydrocarbon radicals are united by the oxygen atom: R—O—R′.

Radicals can be similar or dissimilar (if the radicals are dissimilar, the ethers are said to be *mixed*), and they can be open-chain, cyclic or aromatic.

The names of ethers are usually composed from those of radicals. For example, $CH_3—O—C_2H_5$ is methyl ethyl ether, and $CH_2=CH—O—C_2H_5$, vinyl ethyl ether. If the radicals are symmetrical, **di-** is prefixed to the name, e.g., $C_6H_5—O—C_6H_5$ is diphenyl ether (the prefix is sometimes dropped). There are also names derived from hydrocarbons in which one hydrogen atom is replaced by an alkoxy group:

$CH_3—O—CH_2—CH_3$ — Methoxy ethane

$C_6H_5—O—CH_3$ — Methoxybenzene

Trivial names are also used: phenolic methyl ether $C_6H_5OCH_3$ is called *anisole*, while phenolic ethyl ether $C_6H_5OC_2H_5$, *phenetole*.

The isomerism of ethers is caused by the structure of radicals

$CH_3—O—CH_2—CH_2—CH_3$ — Methyl propyl ether

$CH_3—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ — Methyl isopropyl ether

and by the composition of radicals:

$CH_3—CH_2—O—CH_2—CH_3$ — Diethyl ether

$CH_3—O—CH_2—CH_2—CH_3$ — Methyl propyl ether

Saturated ethers are isomeric to saturated monohydric alcohols, e.g., $CH_3—O—CH_3$ and $CH_3—CH_2—OH$. They have the general formula of $C_nH_{2n+2}O$.

Physical properties. The boiling points of ethers are lower than those of the isomeric alcohols and phenols, e.g.,

	Boiling point, °C		Boiling point, °C
$CH_3—O—CH_3$ . . .	−23.7	CH_3CH_2OH . . .	78.3
$C_6H_5—O—CH_3$ . . .	155	$CH_3C_6H_4OH$ . . .	191

This is because ethers do not form hydrogen bonds and do not associate, as is the case with alcoholic molecules. Ethers, unlike lower alcohols, do not mix with water in all proportions, but the first representatives of the series are partially water-soluble (e.g., water-solubility of diethyl ether is 7 per cent). Ethers are good solvents of organic substances. Their density is less than unity, and they have a pleasant odour.

10.13. Preparation Methods. The following reactions can be used for obtaining ethers:

1. Alcohol dehydration, which is the most important industrial method of preparing ethers (see Sec. 10.4):

$$2R—OH \xrightarrow[\text{heat}]{H_2SO_4;} R—O—R+H_2O$$

Only symmetrical ethers can be obtained by this reaction, because a mixture of three ethers that is difficult to separate is obtained if two different alcohols are taken.

2. The most important method of obtaining ethers is the *Williamson synthesis*, i.e., the action of alkoxides on alkyl halides. The method can be used for obtaining both symmetrical and unsymmetrical ethers:

$$C_2H_5ONa+CH_3I \longrightarrow C_2H_5—O—CH_3+NaI$$
$$C_6H_5ONa+C_2H_5Br \longrightarrow C_6H_5—O—C_2H_5+NaBr$$

Dialkyl sulphates can be used instead of alkyl iodides, especially for obtaining phenolic ethers:

$$C_6H_5ONa+\begin{matrix}CH_3O\\ \\ CH_3O\end{matrix}\!\!>SO_2 \longrightarrow C_6H_5OCH_3+CH_3OSO_3Na$$

3. The addition of alcohols to alkenes. The reaction occurs in an acid medium in the presence of boron trifluoride. The addition direction corresponds to Markovnikov's rule:

$$CH_3—CH=CH_2+HOC_2H_5 \xrightarrow{BF_3} CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—C_2H_5$$

Ethyl isopropyl ether

4. Alkyl vinyl ethers are obtained by heating (150°C) acetylene with alcohols and solid alkali at a pressure of 15-16 kg/cm² (Favorsky-Shostakovsky reaction, 1943):

$$CH{\equiv}CH+HOCH_2{-}CH_3 \longrightarrow \underset{\text{Vinyl ethyl ether}}{CH_2{=}CH{-}O{-}C_2H_5}$$

The reaction can be carried out also in an acid medium in the presence of mercuric salts (Favorsky, 1887), similar to water addition.

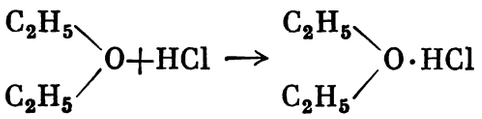
10.14. Chemical Properties. Ethers are considerably less reactive than alcohols. The oxygen-carbon bond is very strong, and it is cleaved with difficulty.

1. A characteristic reaction of ethers is their decomposition when they are heated with hydrogen iodide (iodine becomes bound with the lower radical):

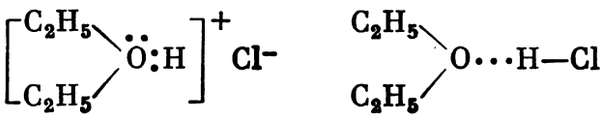
$$C_6H_5O{-}CH_3+HI \longrightarrow C_6H_5OH+CH_3I$$

Neither aqueous alkaline solutions nor dilute acids cause decomposition.

2. Strong acids with ethers yield addition products:



The structure of *oxonium salts* I is usually imparted to these compounds, although the absence of electric conductivity contradicts such a formula and gives rise to the assumption that addition occurs at the expense of the hydrogen bond (II):



I II

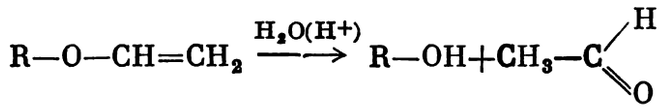
3. Many ethers readily undergo *autooxidation* on storage as they come into contact with air, and especially in the presence of light. The process occurs slowly with the participation of molecular oxygen. In this case, hydroperoxides are formed, e.g.,

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 \xrightarrow{O_2} \underset{\text{Hydroperoxide of diethyl ether}}{CH_3{-}\overset{\overset{OOH}{|}}{CH}{-}O{-}CH_2{-}CH_3}$$

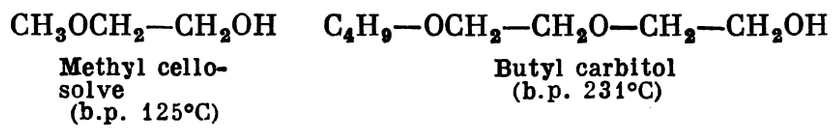
Peroxide compounds are explosive, especially when they are heated. When ether is being distilled, nonvolatile peroxide accumulates in the residue and can cause an explosion. Therefore, prior to distillation, ether should be washed with caustic soda or is treated with reducing agents (Na_2SO_3, $FeSO_4$, etc.) to remove peroxide compounds.

4. Vinyl ethers tend to undergo polymerization and are important intermediates for producing high-molecular-weight compounds.

5. Vinyl ethers, unlike saturated ethers, are readily hydrolyzed in an acid medium, and acetaldehyde is obtained instead of the unstable vinyl alcohol (see Sec. 10.5):

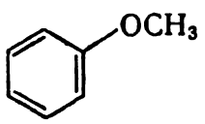


Ethers are often employed as a medium for carrying out various reactions, because they are good solvents of organic substances and are chemically stable; particular use is made of diethyl ether and cyclic ethers: tetrahydrofuran and dioxane. High-boiling monoalkyl ethers of ethylene glycol, *Cellosolves*, and of diethylene glycol, *Carbitols*, are used for dissolving cellulose ethers:

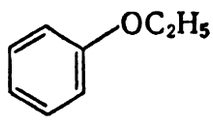


10.15. Important Individual Ethers. *Diethyl ether* (*ethyl ether*, simply "*ether*", *sulphuric ether*) is a liquid with characteristic odour; its b.p. is 34.6°C, m.p., —116.3°C, and d_4^{20}, 0.714. It is readily flammable, its vapours form an explosive mixture with air, and it is capable of undergoing autooxidation. Great care must be taken when storing and handling it. It is used as a solvent of many organic substances. Ether acts as an anesthetic, and it is employed in surgeries.

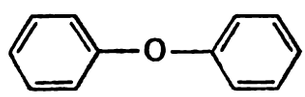
Ethers of phenols and naphthols have a peculiar odour, and therefore they are used in perfumery. The most important ones are methyl ether (*anisole*) and ethyl ether (*phenetole*), which are used as solvents and in synthesizing dyes, medicinals, etc.:



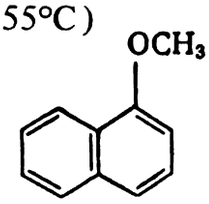
Anisole (b.p. 155°C)



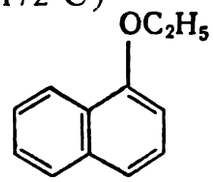
Phenetole (b.p. 172°C)



Diphenyl ether (b.p. 259°C, the odour of geranium)

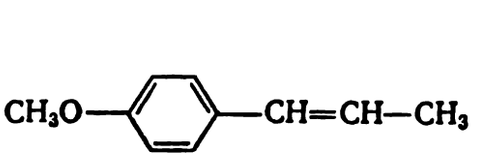


Nerolin (m.p. 72°C, b.p. 275°C, the odour of an orange)

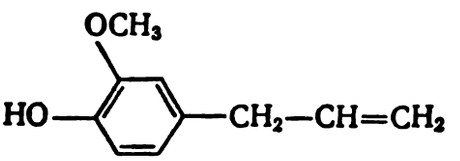


New nerolin (m.p. 37°C, b.p. 275°C, the odour of acacia)

Phenolic ethers which contain an unsaturated side chain are widely distributed in nature. For example, *anethole* is found in anise oil, and *eugenol*, in clove oil.

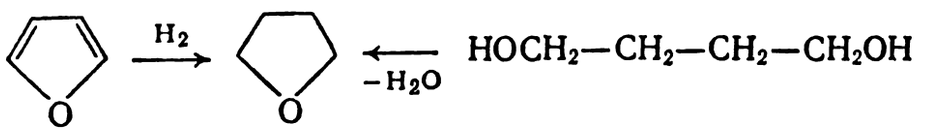


Anethole



Eugenol

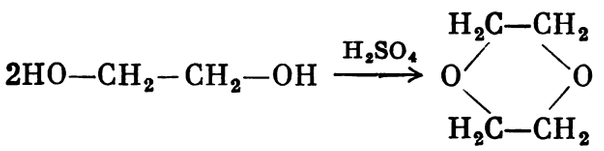
Tetrahydrofuran (*tetramethylene oxide*) is a cyclic ether, a liquid having a b.p. of 66°C, and is water-miscible. It is obtained by hydrogenating the five-membered furan heterocycle or dehydrating 1,4-butanediol:



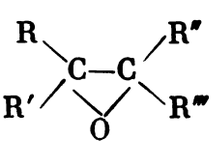
Furan Tetrahydrofuran 1,4-Butanediol

It is often used as a medium for organic reactions, as a solvent in reducing lithium by aluminium hydride, and in Grignard's reactions instead of diethyl ether.

Dioxane is a liquid whose b.p. is 101.5°C, and d_4^{20}, 1.03; it mixes with water, ether and benzene. It is a good solvent of organic and many inorganic substances. It is poisonous, and forms explosive compounds on storage. It is obtained from ethylene glycol under the action of sulphuric acid:

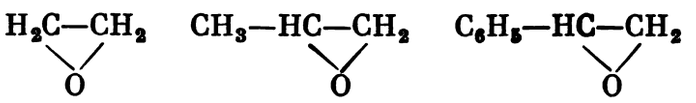


10.16. Epoxides. Cyclic ethers having a three-membered (α-oxide) ring are known as epoxides (the prefix "epi" is used for denoting the neighbouring positions). They are also called *alkene oxides*. The formula of these compounds in its general form can be written as:



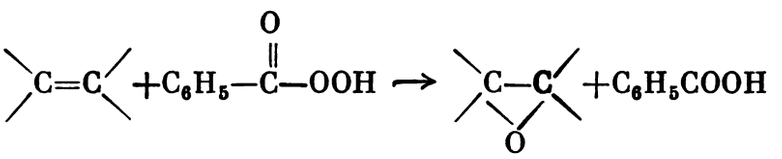
where R, R′, R″ and R‴ are hydrogen, identical or different radicals.

The following compounds can be given as examples of epoxides, and their names show how epoxide names are formed:



Ethylene oxide | Propylene oxide | Styrene oxide

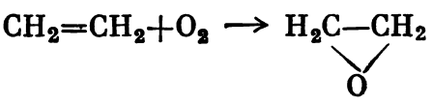
The most important method of obtaining epoxy compounds is by *Prilezhaev's reaction*, i.e., by the action of percarboxylic acids (e.g., perbenzoic acid) on olefins:



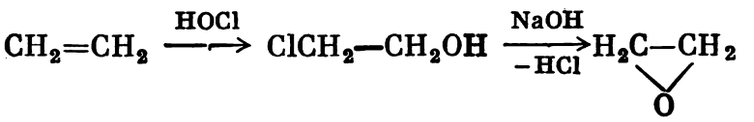
Epoxides, unlike open-chain ethers and cyclic ethers with large rings, are chemically active substances. Their three-membered ring, like cyclopropane, is unstable and readily opens under the action of various reagents. Characteristic examples are the addition reactions of nucleophilic reagents, which are usually carried out in an acid medium.

The most important representative of epoxy compounds is *ethylene oxide*. It is a colourless volatile liquid whose b.p. is 10.7°C and d_4^{20}, 0.89, and it is well-soluble in water. It is stored in steel cylinders under pressure.

The main industrial method of obtaining it is by oxidizing ethylene by atmospheric oxygen while heating it in the presence of a silver catalyst:

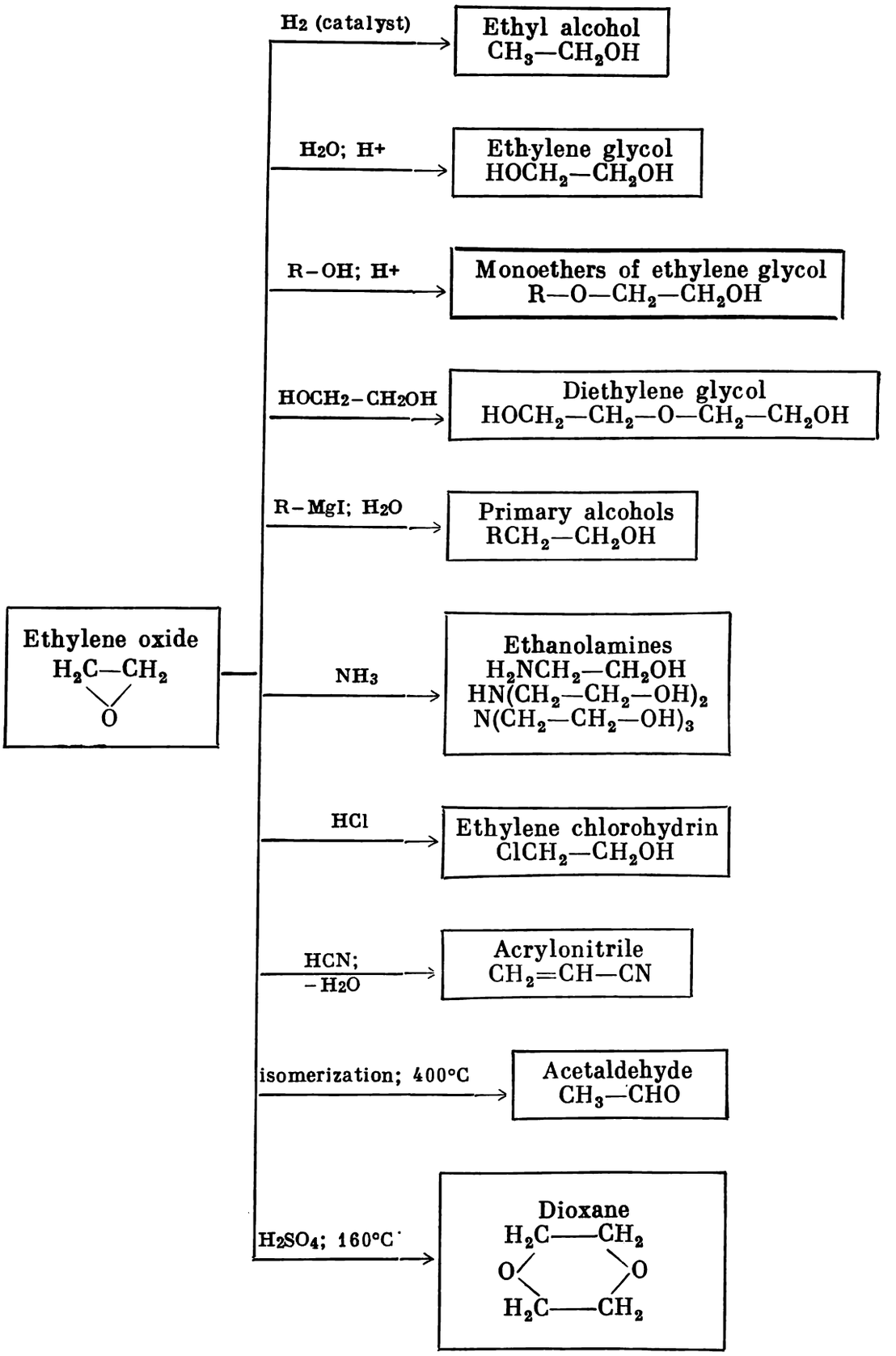


In another, older industrial method, ethylene is converted into ethylene chlorohydrin, while the latter, into ethylene oxide under the action of concentrated alkali:



Ethylene oxide is one of the most important intermediate products of the organic synthesis industry. The most important directions in which it is used are given in Diagram 10.1. Ethylene oxide is employed also for disinfecting transportation means and living quarters.

DIAGRAM 10.1. **Industrial Use of Ethylene Oxide**



ORGANIC PEROXIDE COMPOUNDS

10.17. Methods of Preparing Alkyl Peroxides. Chemical Properties. Organic peroxides can be regarded as the organic derivatives of hydrogen peroxide HO—OH in which one hydrogen atom (*hydroperoxides*) or both hydrogen atoms (*alkyl peroxides*) are replaced by alkyl radicals:

RO—OH	RO—OR
Hydroperoxides	Alkyl peroxides

Preparation methods. 1. Autooxidation. At the end of the last century, A. N. Bakh ascertained that some organic substances are autooxidized when they come into contact with air. The mechanism of autooxidation reactions was revealed by N. N. Semyonov (1927); they are free-radical chain reactions. The reaction can be initiated by mercury vapours, ultraviolet light, etc.:

$$R{-}H + X\cdot \longrightarrow R\cdot + HX \quad \text{(chain initiation)}$$

$$\text{(chain propagation)} \quad \begin{cases} R\cdot + O_2 \longrightarrow R{-}O{-}O\cdot \\ R{-}O{-}O\cdot + H{-}R \longrightarrow R{-}O{-}O{-}H + R\cdot \end{cases}$$

$$\left.\begin{array}{l} R\cdot + R\cdot \longrightarrow R{-}R \\ R{-}O{-}O\cdot + R\cdot \longrightarrow R{-}O{-}O{-}R \end{array}\right\} \text{(chain termination)}$$

The free radical initiating the reaction chain abstracts the hydrogen atom of the most reactive group (CH or CH_2) and forms a free radical, which binds molecular oxygen.

Alkanes and cycloalkanes are oxidized rather readily, and the tertiary carbon atom is mainly affected:

$$(CH_3)_3CH \xrightarrow{O_2} (CH_3)_3C{-}OOH$$

Isobutane — *tert*-Butyl hydroperoxide

In alkenes, the carbon atom in the allylic position is readily oxidized:

$$CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow{O_2} CH_3{-}\underset{\displaystyle OOH}{\underset{|}{CH}}{-}CH{=}CH_2$$

1-Butene — 1-Butenyl hydroperoxide

In aromatic hydrocarbons, the carbon atom of a side chain that is the closest to the benzene nucleus is oxidized most readily (e.g., the formation of cumyl hydroperoxide, see Sec. 10.8).

2. Addition of hydrogen peroxide to olefins:

$$(CH_3)_2C{=}CH_2 + HO{-}OH \longrightarrow (CH_3)_2\underset{\displaystyle OOH}{\underset{|}{C}}{-}CH_3$$

3. Alkylation of hydrogen peroxide by alkyl sulphates in the presence of alkalies:

$$(CH_3O)_2SO_2+HO-OH \xrightarrow{KOH} \underset{\text{Methyl hydroperoxide}}{CH_3-OOH}+CH_3O-OSO_2K+H_2O$$

$$CH_3-OOH+(CH_3O)_2SO_2 \xrightarrow{KOH} \underset{\text{Methyl peroxide}}{CH_3O-OCH_3}+CH_3O-OSO_2K+H_2O$$

4. *tert*-Butyl hydroperoxide and *tert*-butyl peroxide can be obtained in the reaction between *tert*-butyl alcohol and hydrogen peroxide in an acid medium:

$$(CH_3)_3C-OH+HO-OH \xrightarrow{H^+} \underset{\text{\textit{tert}-Butyl hydroperoxide}}{(CH_3)_3C-OOH}$$

$$(CH_3)_3C-OOH+(CH_3)_3C-OH \longrightarrow \underset{\text{\textit{tert}-Butyl peroxide}}{(CH_3)_3C-O-O-C(CH_3)_3}+H_2O$$

Chemical properties. Hydroperoxides are more acidic than alcohols. For example, they form salts when they react with concentrated alkaline solutions. Hydroperoxides are oxidizing agents, e.g., they readily react with hydrogen iodide, evolving iodine. This reaction is used for the quantitative iodometric determination of hydroperoxides:

$$CH_3-OOH+2HI \longrightarrow CH_3OH+I_2+H_2O$$

Peroxides react with hydrogen iodide with greater difficulty than hydroperoxides. They are readily decomposed into free alkoxyl radicals:

$$(CH_3)_3C-O-O-C(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

Hydroperoxides of lower alkyls are unstable explosive liquids. For example, *tert*-butyl hydroperoxide (b.p. 33°C at 17 mm Hg) decomposes with an explosion when it is heated above 100°C; a free alkoxyl radical is formed when it is carefully heated:

$$(CH_3)_3C-OOH \longrightarrow (CH_3)_3CO\cdot+\cdot OH$$

Free alkoxyl radicals are used as initiators of chain reactions of polymerization.

Peroxide compounds of acids and their derivatives, *peracids* and *acyl peroxides*, are described in Sec. 12.17.

Chapter 11

ALDEHYDES AND KETONES

The functional group of this type of compounds is the carbonyl group $\rangle C{=}O$. Compounds in which the carbonyl group is united with one organic radical and with the hydrogen atom, $R{-}\overset{\overset{O}{\|}}{C}{-}H$, are called *aldehydes*, while the group $-\overset{\overset{O}{\|}}{C}{-}H$ (or $-CHO$), the *aldehyde group*. Compounds in which the carbonyl group is attached to two hydrocarbon radicals, $R{-}\overset{\overset{O}{\|}}{C}{-}R'$, are known as *ketones*, while the group $\rangle C{=}O$, the *keto group*.

The molecule of a carbonyl compound can contain one or several carbonyl groups. Carbonyl compounds can be saturated, unsaturated (if the radical has a multiple bond), aromatic or heterocyclic, depending on the radical which is joined to the carbonyl group.

11.1. Isomerism and Nomenclature. Isomerism and nomenclature of aldehydes. The isomerism of aldehydes is engendered by the structure of the hydrocarbon radical.

Common names for aldehydes are those derived from the corresponding carboxylic acids: formaldehyde, acetaldehyde, butyraldehyde.

In rational nomenclature, aldehydes with a branched chain are regarded as acetaldehyde derivatives. By modern international rules, for aldehydes names are derived from the corresponding hydrocarbons, and the presence of the aldehyde group is denoted by the suffix **al**. The carbon atom of the aldehyde group determines the beginning of numeration. The names of aldehydes and ketones are given in Table 11.1.

Isomerism and nomenclature of ketones. The isomerism of ketones is engendered by the structure of radicals and the position of the keto group, which can be located in different positions.

TABLE 11.1. **Names of Aldehydes and Ketones**

Formula	Name	
	trivial or rational	in modern international nomenclature
	Aldehydes	
$H-CHO$	Formaldehyde	Methanal
CH_3-CHO	Acetaldehyde	Ethanal
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CHO$	Isovaleraldehyde (isopropyl acetaldehyde)	3-Methylbutanal
$CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-CHO$	Trimethylacetaldehyde	2,2-Dimethylpropanal
$CH_2=\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CHO$	Methacrylaldehyde	2-Methylpropenal
$C_6H_5-CH_2-CHO$	Phenylacetaldehyde	2-Phenylethanal
	Ketones	
$CH_3-\underset{\displaystyle O}{\underset{\Vert}{C}}-CH_3$	Dimethylketone, acetone	Propanone
$CH_3-\underset{\displaystyle O}{\underset{\Vert}{C}}-CH_2-CH_2-CH_3$	Methyl propyl ketone	2-Pentanone
$CH_3-\underset{\displaystyle O}{\underset{\Vert}{C}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	Methyl isopropyl ketone	3-Methyl-2-butanone
$CH_3-CH_2-\underset{\displaystyle O}{\underset{\Vert}{C}}-CH_2-CH_3$	Diethyl ketone	3-Pentanone
$CH_3-\underset{\displaystyle O}{\underset{\Vert}{C}}-CH_2-CH=CH_2$	Methyl allyl ketone	4-Penten-2-one

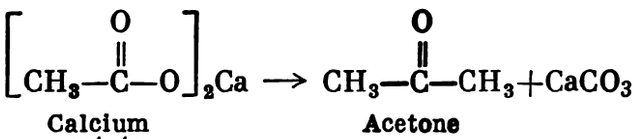
In rational nomenclature, the name of a ketone is composed from the names of radicals attached to the carbonyl group, and the ending *ketone* is added. By modern international rules, the keto group is denoted by the suffix **one** and by a numeral which indicates the number of the carbon atom of the carbonyl group. The numeration begins from the chain end which is the closest to the keto group.

Aldehydes and ketones are isomeric. The general formula of saturated aldehydes and ketones is $C_nH_{2n}O$.

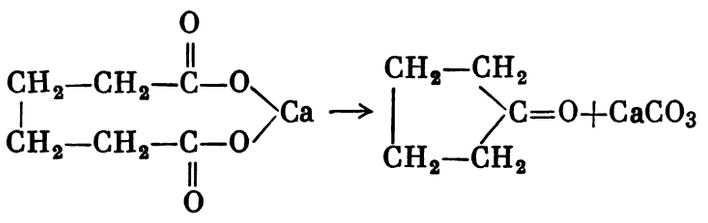
11.2. Preparation Methods. The following methods are used for obtaining carbonyl compounds.

1. From alcohols. In oxidation, primary alcohols yield aldehydes, and secondary ones, ketones (see Sec. 10.4). The method is often used in the laboratory (the oxidizing agent is the chromic-acid mixture) for obtaining readily volatile aldehydes and ketones (formaldehyde, acetaldehyde, acetone, cyclohexanone), which move away from the reaction sphere as they are formed. In industrial methods, the oxidizing agent is atmospheric oxygen in the presence of a catalyst. Carbonyl compounds are obtained also by catalytically dehydrogenating alcohols (see Sec. 10.4).

2. Decarboxylation of carboxylic acids and their salts. The "dry distillation" of the calcium (barium) salts of carboxylic acids is a common method for obtaining any ketones. The salts of monobasic acids yield open-chain ketones, while those of dibasic acids, cyclic ketones. The molecule of the ketone being formed contains one carbon atom less than that of the initial salt:

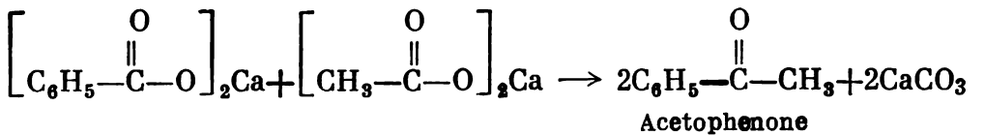


Calcium acetate — Acetone



Calcium adipate — Cyclopentanone

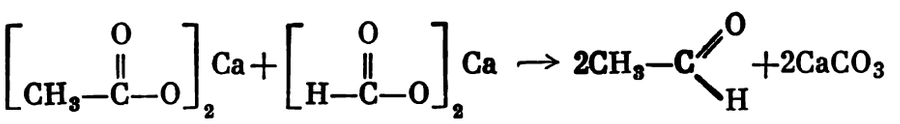
Unsymmetrical ketones are obtained from a mixture of salts of two different acids:



Acetophenone

Acetone $(CH_3)_2C{=}O$ and benzophenone $(C_6H_5)_2C{=}O$ are obtained at the same time in this reaction.

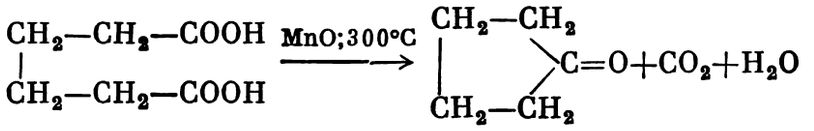
If one of the components is formate, aldehydes are formed:



Calcium acetate — Calcium formate

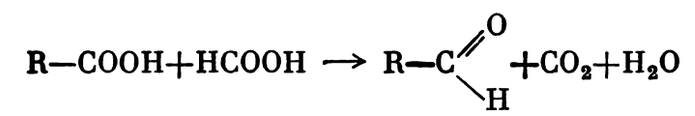
A more advanced method of obtaining ketones from acids is by passing acid vapours over a catalyst. Manganous and thorium oxides

are regarded as good catalysts for the reaction:

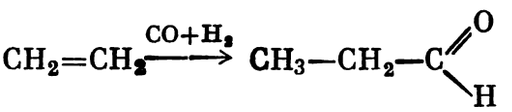


Cyclopentanone

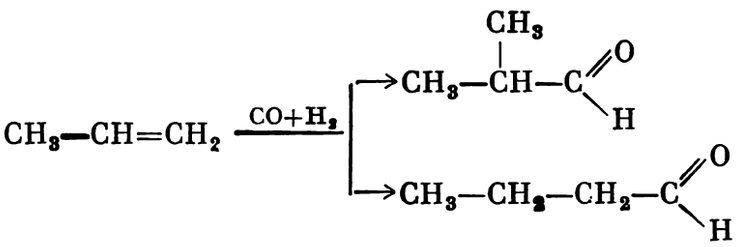
Aldehydes are obtained by using a mixture of formic acid and some other acid:



3. Alkene hydroformylation (*Oxo synthesis*). In this method, aldehydes are obtained when a mixture of carbon monoxide and hydrogen (water gas) is added to olefins. The reaction is carried out in the presence of dicobalt octacarbonyl, $[Co(CO)_4]_2$, at 140°C and a pressure of 200 kg/cm^2:



Aldehydes having normal and branched chains are formed from ethylene homologues:



This reaction makes it possible to obtain organic oxygen-containing substances, which are capable of undergoing many further transformations, from the products of the oil-refining industry.

4. Oxidation of hydrocarbons by atmospheric oxygen in the presence of catalysts. The method is used industrially and is becoming of ever greater importance. That is how acetaldehyde is obtained from ethylene (see Sec. 11.5), and acetone, from cumene (see Sec. 10.8).

5. From acetylene hydrocarbons by hydration with the aid of Kucherov's reaction (see Sec. 5.4). This method is modified by using the sulphopolystyrene ionite impregnated with mercury salts as a catalyst (Ingold, 1953).

Another way of obtaining aldehydes and ketones from acetylene hydrocarbons is by means of vinyl ethers:

$$CH{\equiv}CH+CH_3OH \xrightarrow[\text{(pressure)}]{KOH} CH_2{=}CH{-}OCH_3 \xrightarrow[-CH_3OH]{H_2O(H^+)} CH_3{-}C(=O){-}H$$

$$R{-}C{\equiv}CH+CH_3OH \xrightarrow{KOH} R{-}C(OCH_3){=}CH_2 \xrightarrow[-CH_3OH]{H_2O(H^+)} R{-}C(=O){-}CH_3+CH_3OH$$

6. The hydrolysis of dihalogen derivatives containing both halogen atoms attached to one carbon atom in the presence of acids or bases. If both halogen atoms are attached to the primary carbon atom, aldehydes are formed, and if to the secondary one, ketones are formed:

$$CH_3{-}C(Cl)(Cl){-}H \xrightarrow{\text{hydrolysis}} \left[CH_3{-}C(OH)(OH){-}H\right] \xrightarrow[-H_2O]{} CH_3{-}C(=O){-}H$$

$$CH_3{-}C(Cl)(Cl){-}CH_3 \xrightarrow{\text{hydrolysis}} \left[CH_3{-}C(OH)(OH){-}CH_3\right] \xrightarrow[-H_2O]{} CH_3{-}C(=O){-}CH_3$$

7. The reduction of acyl chlorides. Carboxylic acids are reduced with difficulty (with greater difficulty than aldehydes), while strong reducing agents engender primary alcohols and even hydrocarbons. Acyl chlorides are reduced considerably more readily with the formation of aldehydes:

$$R{-}C(=O){-}Cl \xrightarrow[(130^\circ C)]{H_2/Pd} R{-}C(=O){-}H + HCl$$

To prevent aldehyde from being reduced further, the palladium catalyst is partially poisoned with sulphur. This is a laboratory method.

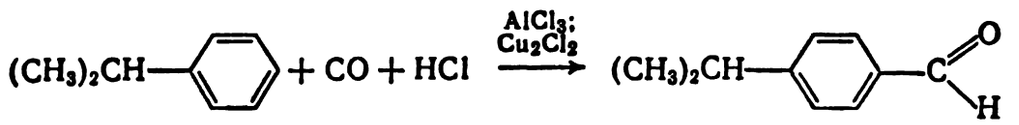
8. The synthesis of aromatic ketones by the Friedel-Crafts reaction from aromatic hydrocarbons and acid chlorides in the presence of aluminium chloride (acylation reaction):

$$C_6H_6 + Cl{-}C(=O){-}CH_3 \xrightarrow{AlCl_3} C_6H_5{-}C(=O){-}CH_3 + HCl$$

Acetophenone

9. The direct introduction of the aldehyde group into the benzene nucleus. The formylation reaction can be effected by Gattermann's

method as a mixture of carbon monoxide and hydrogen chloride acts on aromatic hydrocarbons in the presence of aluminium chloride and cuprous salts. The reaction occurs more readily with benzene homologues, and *para*-isomers are mainly formed:



p-Isopropylbenzaldehyde (cuminal)

11.3. Structure of the Carbonyl Group. Physical Properties of Aldehydes and Ketones. In the functional group of aldehydes and ketones the carbon-oxygen bond is a double one (a four-electron one). The carbon atom of the carbonyl group is in the state of sp^2 hybridization, and its configuration is planar (Fig. 11.1*a*). Since oxygen

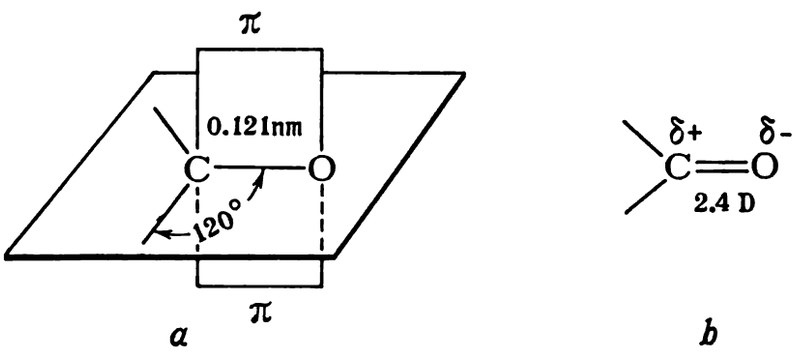


Fig. 11.1. Structure of the carbonyl group

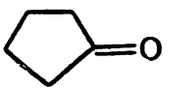
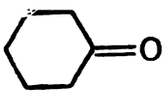
is more electronegative than carbon, the C=O bond, unlike the C=C bond, is highly polarized as a result of the displacement of the electron density of the π-bond towards oxygen (Fig. 11.1*b*).

The dipole moments of aldehydes and ketones approximate 2.7 D, i.e., they are much higher than those of alcohols, which have a dipole moment of the order of 1.7 D.

The polarity of a carbonyl group affects the physical properties. Many aldehydes and ketones are well soluble in water. Lower aldehydes and ketones (acetaldehyde, acetone) mix with water in all proportions. The boiling points of the lower members of the aldehyde and ketone series are higher than those of the corresponding hydrocarbons and lower than those of the corresponding alcohols; this fact indicates the absence of considerably great molecular association in carbonyl compounds. Lower aldehydes have a pungent odour, while many higher aldehydes and ketones have a pleasant flowery odour, and therefore they are used in perfumery.

The physical properties of some aldehydes and ketones are given in Table 11.2.

TABLE 11.2. **Physical Properties of Some Aldehydes and Ketones**

Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Formaldehyde	H—CHO	—92	—20	0.81 (at —20°C)
Acetaldehyde	CH_3—CHO	—121	+21	0.80
Propionaldehyde	CH_3—CH_2—CHO	—81	49	0.807
Acrolein	CH_2=CH—CHO	—87	52	0.84
Benzaldehyde	C_6H_5—CHO	—26	180	1.05 (at 15°C)
Acetone	CH_3—C(=O)—CH_3	—94	56	0.792
Methyl ethyl ketone	CH_3—C(=O)—C_2H_5	—86	80	0.805
Cyclopentanone		—58	130	0.94
Cyclohexanone		—40.5	156	0.94
Acetophenone	C_6H_5—C(=O)—CH_3	+20	202	1.02

11.4. Chemical Properties. The polarity of a carbonyl group also determines its reactions. The carbonyl group is one of the most reactive groups. Its characteristic features are: (1) addition reactions along its double bond; (2) replacement of the carbonyl oxygen by different nitrogen-containing groupings; (3) condensation reactions.

Addition reactions. Additions to a carbonyl group are *nucleophilic* processes. They begin with the interaction between positively charged carbonyl carbon and the free electron pair of the nucleophile (they occur slow):

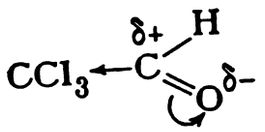
$$>C^{\delta+}=O^{\delta-} + :X^- \xrightarrow{\text{slow}} -\overset{X}{\underset{}{C}}-O^-$$

The second stage consists in the addition of the proton (or another cation) to the anion formed (this occurs fast):

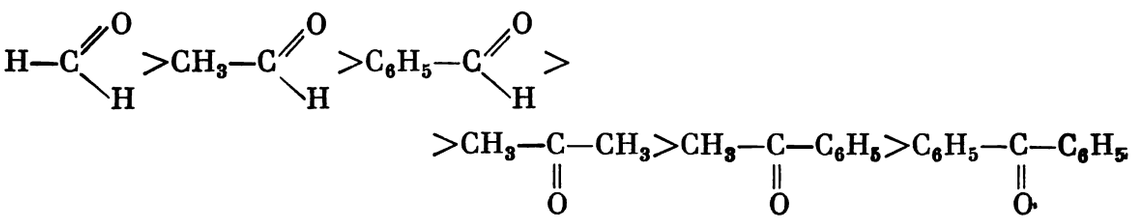
$$-\overset{X}{\underset{}{C}}-O^- + H^+ \xrightarrow{\text{fast}} -\overset{X}{\underset{}{C}}-OH$$

The activity of carbonyl compounds and the reaction rate depend on the intensity of the positive charge on the carbon atom of a carbonyl group. The higher the charge, the faster is the nucleophilic particle added.

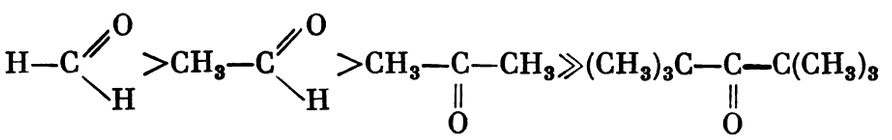
Different substituents at the carbonyl carbon atom either increase or reduce the electron density of this atom. The electron-accepting substituents reduce the electron density, i.e., they increase the positive charge of the carbonyl carbon atom, as a result of which the addition of nucleophilic reagents occurs more readily and more rapidly. For example, the positive charge of the carbonyl carbon atom is higher in trichloroacetaldehyde (chloral) than in acetaldehyde, and therefore the aldehyde group in chlorine-substituted aldehyde is more active:



Conversely, electron-donating substituents retard the addition reaction, because they increase the electron density on the carbonyl carbon atom, reducing its positive charge. Alkyls are electron donors, and therefore the positive charge of the carbonyl carbon atom is lower in acetaldehyde than in formaldehyde. The electron-donating properties of aryl are even more pronounced, and therefore aromatic aldehydes and ketones are less active than aliphatic ones. Thus, carbonyl compounds can be arranged in the following series according to the diminution in their activity:

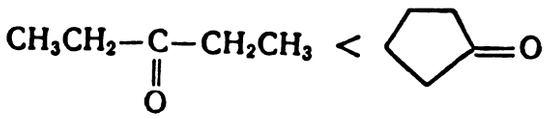


The reactivity of a carbonyl group is affected also by the size of the radicals attached to it: the larger they are, the more difficult it is for a reagent to reach the carbonyl carbon atom. The aldehyde group is more susceptible to attack than the keto group, because the hydrogen atom hardly impedes the approach of reagents, and therefore aldehydes are more active than ketones:

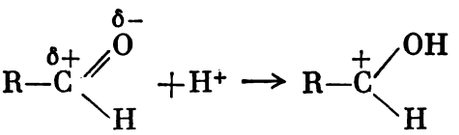


Acyclic ketones react more slowly than their cyclic analogues owing to the steric hindrances which alkyl groups can create for

the reagent as it approaches a carbonyl group:



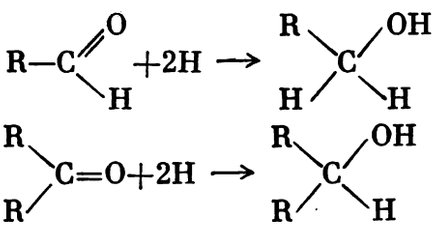
An acid medium (acidic catalysis) is required for many reactions of aldehydes and ketones. Proton addition causes an increase in the positive charge on the carbonyl carbon atom:



Different polar reagents are added to the carbonyl group according to the general scheme given on page 216.

The most important reactions of such a type are given below:

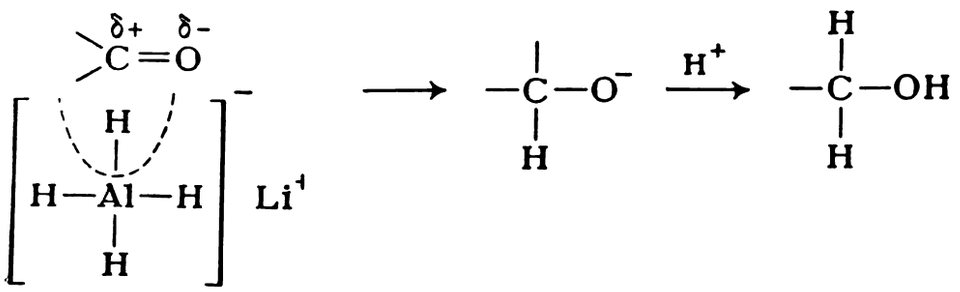
1. Hydrogen addition with the formation of alcohols. Primary alcohols are obtained from aldehydes, and secondary ones, from ketones:



Lithium aluminium hydride and sodium borohydride are effective reducing agents of carbonyl groups. These reducing agents do not affect the double carbon-carbon bond when unsaturated aldehydes are being reduced.

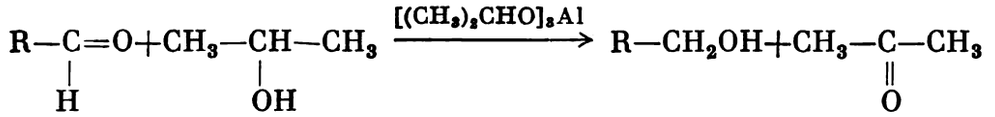
Lithium aluminium hydride is susceptible to the action of moisture and acids. It is used as a solution in dry ether, tetrahydrofuran or pyridine.

In complex hydrides, the hydrogen atom bears a partial negative charge and passes over, together with the bonding electron pair, to the positively charged carbonyl carbon atom. The second hydrogen atom which is required for completing reduction comes not from the reducing agent, but from acid (or other proton solvent) as the reaction mixture decomposes:



The remaining three hydride hydrogen atoms are used for reducing other molecules of the carbonyl compound. Thus, one mole of lithium aluminium hydride reduces four moles of the carbonyl compound.

Good results are also obtained by reducing aldehydes to primary alcohols with the aid of isopropyl alcohol in the presence of aluminium isopropoxide by means of the Meerwein-Ponndorf reaction (acetone, which is also formed, is distilled off):

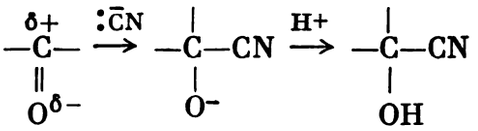


The reaction is used in the laboratory. Like reduction by hydrides, it can be used for reducing unsaturated compounds, and the double carbon-carbon bond is not affected in this case.

The double carbon-carbon bond of unsaturated aldehydes and ketones is reduced under the conditions of catalytic hydrogenation (the catalysts are Ni, Pt, Pd and copper chromite).

2. Addition of hydrogen cyanide. *Cyanohydrins* (hydroxy nitriles or nitriles of α-hydroxy acids) are formed as a result of this reaction.

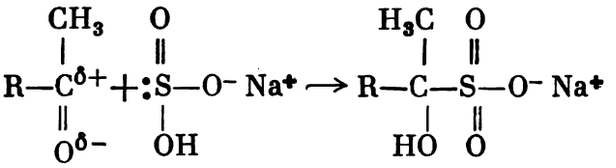
The cyanide ion attacks the carbonyl carbon atom, and the anion then formed binds the proton:



A mixture of a carbonyl compound, sodium cyanide and a smale amount of a strong mineral acid is practically introduced into thr reaction, because hydrocyanic acid does not react owing to its pool dissociation.

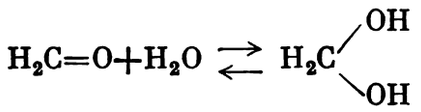
Cyanohydrins are used as intermediates for synthesizing hydroxy acids, amino acids, etc.

3. In an aqueous solution, sodium bisulphite is readily added to aldehydes, methyl ketones and simple cyclic ketones, and then *bisulphite addition compounds* are formed:



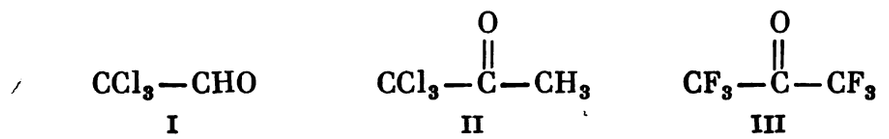
These substances crystallize well and are insoluble in excess sodium bisulphite. They are hydrolyzed in both acidic and basic media, forming initial carbonyl compounds. These properties are used for purifying aldehydes and ketones, and for isolating them from mixtures.

4. Water addition. Formaldehyde readily adds water at room temperature (without a catalyst), forming formaldehyde hydrate:



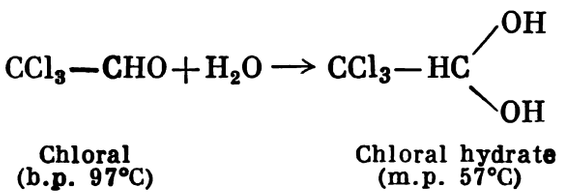
Aldehyde hydrates could not be obtained in a free state. The fact that the reaction is occurring is indicated by the heat evolved as formaldehyde and acetaldehyde dissolve in water. Spectral methods did not indicate the presence of a carbonyl group in aqueous formaldehyde solutions. The spectrum of such a solution is similar to that of glycol.

Halogenated aldehydes and ketones, e.g., chloral I, trichloroacetone II and hexafluoroacetone III



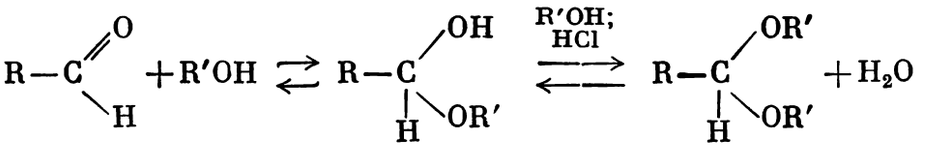
have a greater tendency to add water than unsubstituted ones, and their hydrates can be isolated in a free state.

Chloral hydrate is formed in the following reaction:



Chloral (b.p. 97°C) — Chloral hydrate (m.p. 57°C)

5. Addition of alcohols. Aldehydes can add alcohols. The first to be formed are *hemiacetals*, or partial *gem*-diol* ethers. Absolute ethers of hydrate forms, *acetals*, are obtained when hemiacetals are heated with excess alcohol in the presence of hydrogen chloride:



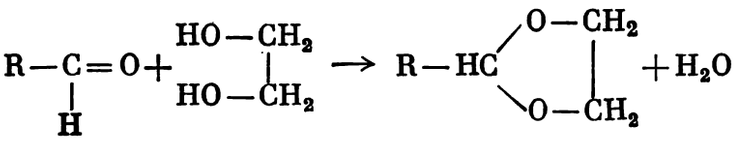
Hemiacetal — Acetal

Acetals are stable and can be separated in a free state. Unlike ordinary ethers, they are hydrolyzed under the action of acids, forming alcohol and aldehyde. They do not decompose in an alkaline medium.

Acetalization is often used for protecting the aldehyde group. Cyclic acetals of ethylene glycol are the most important in this

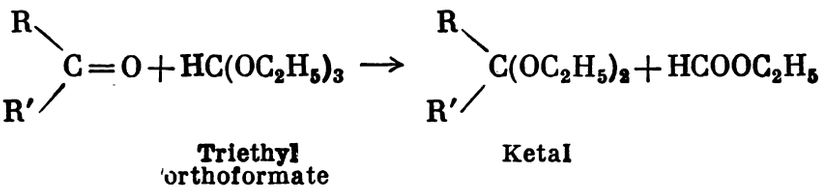
* The prefix *gem*-indicates that two functional groups are attached to one carbon atom.

respect:



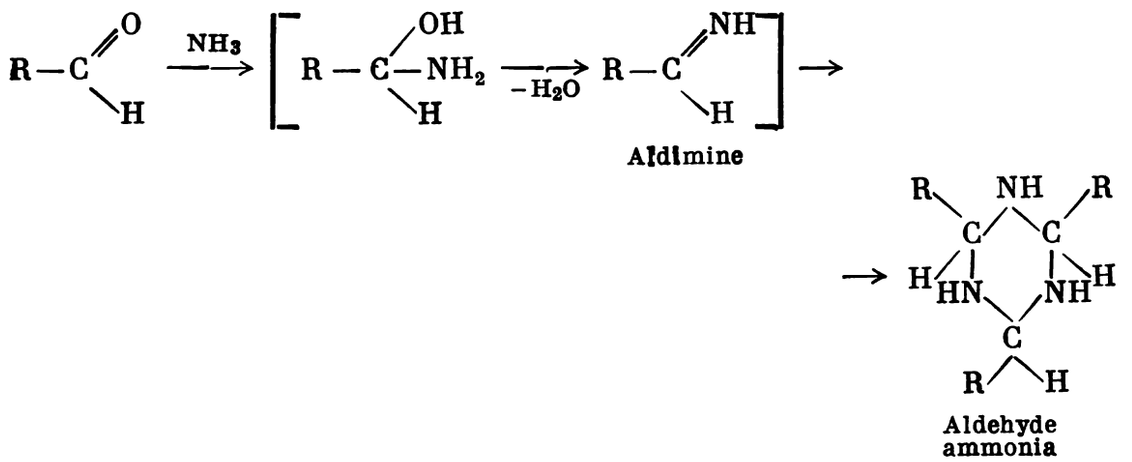
In carrying out some reactions, it is necessary to protect one of the active groups contained in the molecule of a reacting substance from the action of a reagent. To this end, it is at first converted into a group which is stable in a given reaction, but which is readily regenerated after the reaction.

Ketones are not characterized by the reaction of direct interaction with alcohols in which compounds similar to acetals, ketals, are formed. *Ketals* are readily formed in this reaction only with methyl alcohol and ethylene glycol. They are usually obtained in the reaction with orthoformates:



6. Addition of organomagnesium compounds (Grignard's reagents) is among the typical reactions of aldehydes and ketones. This reaction is considered in the chapter "Organoelement Compounds" (see Sec. 17.2).

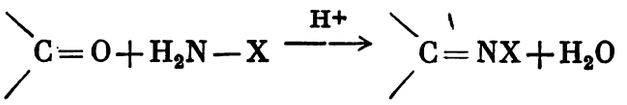
7. Addition of ammonia. This reaction is characteristic of many aldehydes. The first addition products to be formed are poorly stable, and they are readily dehydrated with the formation of *aldimines* and polymerized (trimerized) into *aldehyde ammonias*:



These compounds decompose with the isolation of free aldehyde under the action of dilute mineral acids.

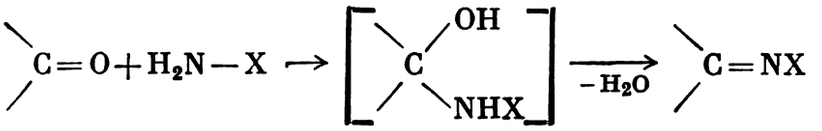
For ketones, the reaction with ammonia occurs with greater difficulty.

Substitution reactions of oxygen of the carbonyl group. 1. Aldehydes and ketones are characterized by reactions with substances which contain the NH_2 group in the molecule. As a result, water is isolated and derivatives containing the grouping $-C=N-X$ are formed:

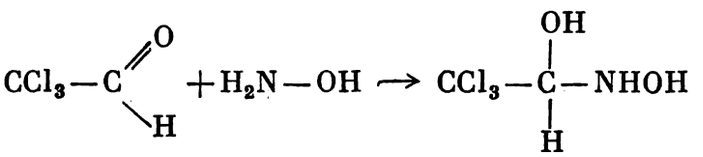


where X is OH, NH_2, etc.

Substitution reactions can be treated in the same way as addition reactions. It can be taken that the ordinary addition of a reagent to a carbonyl group occurs at first, and then water is eliminated:

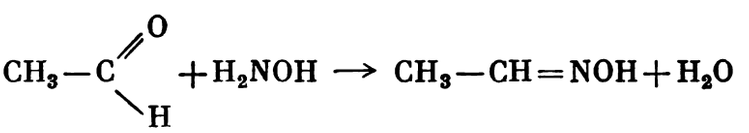


Such an intermediate addition product was isolated as hydroxylamine acted on chloral:

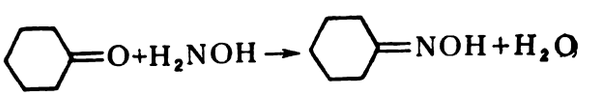


In most cases, intermediate addition products are unstable, and they cannot be trapped.

(a) Reaction with Hydroxylamine. *Aldoximes* and *ketoximes* are formed when hydroxylamine reacts with aldehydes and ketones:



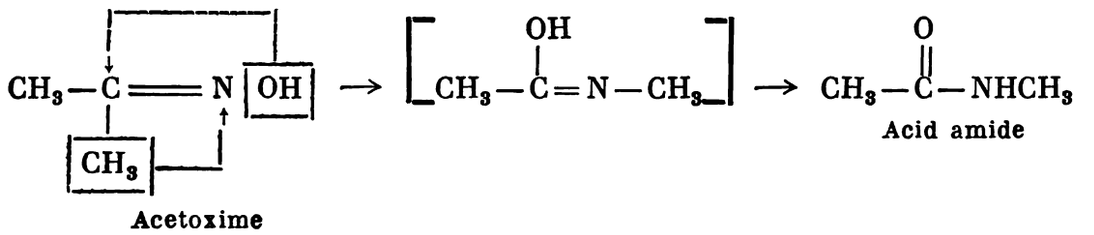
Acetaldehyde oxime



Cyclohexanone oxime

Ketoximes are capable of undergoing a reaction with a change in its chemical structure, i.e., they are capable of undergoing the *Beckmann rearrangement* (1886). This reaction occurs in an acid medium. The rearrangement formally consists in the fact that one of the oxime radicals shifts from carbonyl carbon to nitrogen, while the hydroxyl passes over to carbonyl carbon. Since the hydroxyl

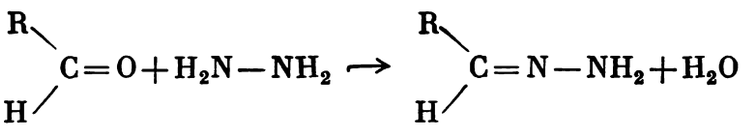
attached to the double bond is unstable (Eltekov's rule), the hydrogen of the hydroxyl group shifts to nitrogen, and then the carbonyl group is formed:



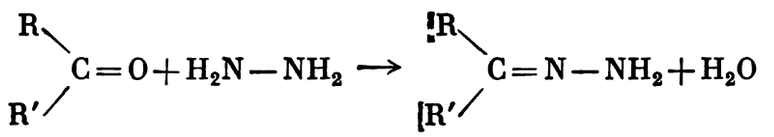
Acetoxime

Acid amide

(b) Reaction with Hydrazine. *Hydrazones* are formed as a result of the action of hydrazine on carbonyl compounds:

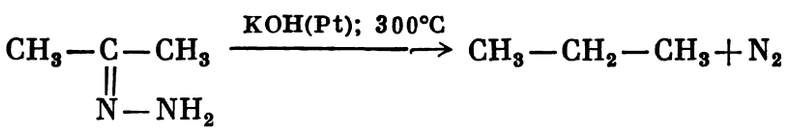


Aldehyde hydrazone

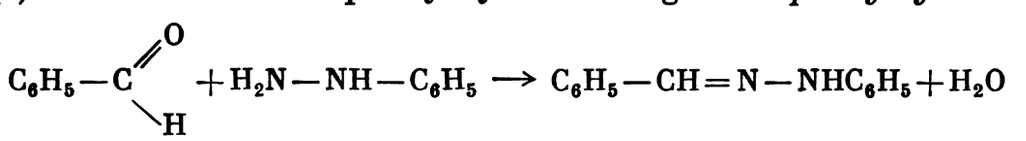


Ketone hydrazone

Hydrocarbons are formed and free nitrogen is liberated when hydrazones are heated with calcium hydroxide in the presence of platinum. This reaction was discovered almost simultaneously by the Russian scientist N.M. Kishner (1911) and by the German scientist L. Wolff (1912). This transformation is known as the Wolff-Kishner reaction:



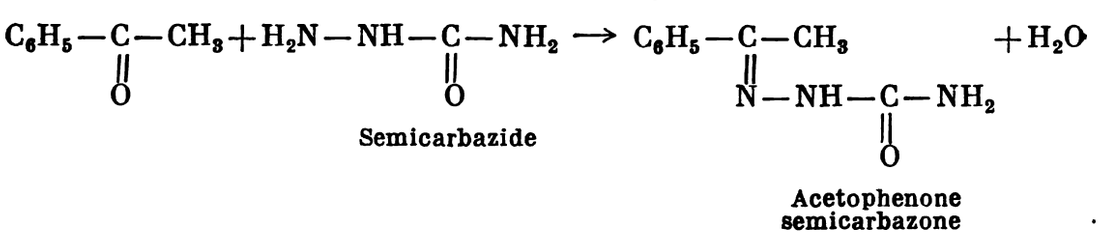
(c) The reaction with phenylhydrazine engenders *phenylhydrazones*:



Phenylhydrazine

Benzaldehyde phenylhydrazone

(d) The reaction with semicarbazide yields *semicarbazones*:

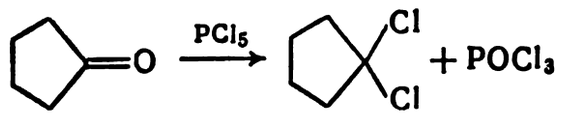


Semicarbazide

Acetophenone semicarbazone

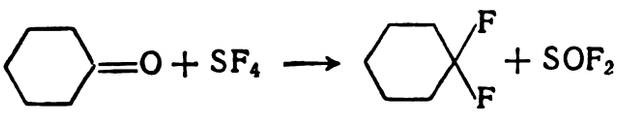
Oximes, hydrazones, phenylhydrazones and semicarbazones are solid crystalline substances with characteristic melting points. This property is used for identifying aldehydes and ketones.

2. Replacement of the carbonyl oxygen by chlorine. The reaction is effected by means of phosphorus pentachloride:



Cyclopentanone — 1,1-Dichlorocyclopentane

3. Replacement of oxygen by fluorine in the reaction with sulphur tetrafluoride:



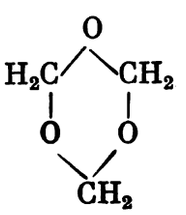
Cyclohexanone — 1,1-Difluorocyclohexane — Thionyl fluoride

Polymerization reactions. In aldehyde polymerization, the double bond of a carbonyl group is ruptured and the oxygen atom of one molecule becomes linked with the carbonyl carbon atom of another. This can result in the formation of linear and cyclic products. For example, a white precipitate gradually falls out when an aqueous formaldehyde solution is allowed to stand. The precipitate is a linear polymer, named *paraform* or *polyoxymethylene*:

$$n\mathrm{CH_2{=}O + H_2O} \longrightarrow \mathrm{HOCH_2[{-}OCH_2{-}]_{n-2}OCH_2OH}$$
$$n = 10\text{-}50$$

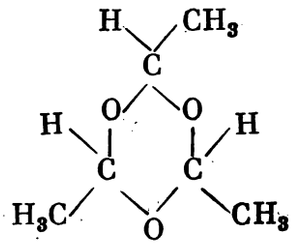
Monomeric formaldehyde is isolated when paraform is heated up to 150°C. Chemists have recently succeeded in polymerizing dry formaldehyde into valuable *polyformaldehyde* of a much higher molecular weight.

When formaldehyde is heated with dilute acid, it becomes polymerized with the formation of cyclic *trioxymethylene*:

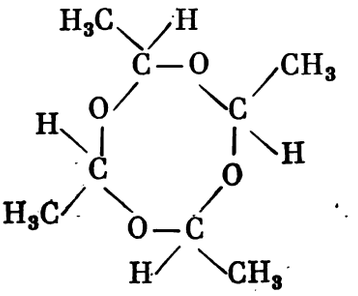


Acetaldehyde forms, under the action of acids (H_2SO_4, HCl), a liquid cyclic trimer known as *paraldehyde* and a solid tetramer

known as *metaldehyde* ("dry alcohol"). The latter is formed when acetaldehyde is polymerized below 0°C:



Paraldehyde (m.p. 10°C, b.p. 124°C)



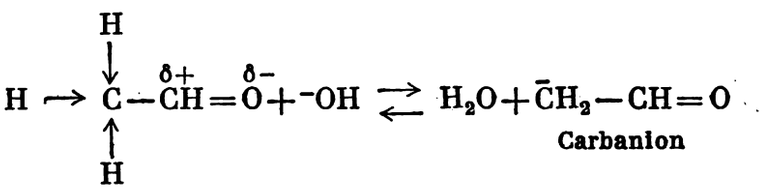
Metaldehyde (sublimes at 112°C)

When these polymers are heated in the presence of dilute mineral acids, they depolymerize with the formation of acetaldehyde.

Aromatic aldehydes with the aldehyde group which is attached directly to the benzene nucleus do not polymerize. Compounds containing an aldehyde group which is far removed from the benzene nucleus act as aliphatic aldehydes.

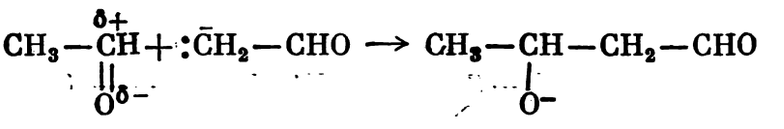
Condensation reactions. In aldehyde and ketone molecules, the hydrogen atoms of the next-to-carbonyl carbon (α-position) acquire a partial positive charge under the action of the carbonyl group and are thus capable of undergoing elimination as a proton. In this case, an aldehyde or ketone is converted into the carbanion. Consequently, aldehydes and ketones are capable of undergoing condensation reactions which occur according to the nucleophilic addition mechanism. These reactions result in the formation of new carbon-carbon bonds.

1. Condensation between two aldehydes. The carbonyl group of one molecule (*carbonyl component*) and α-hydrogen of another molecule (*methylene component*) become involved in the reaction. The molecule of the carbonyl compound turns, under the action of bases, into the carbanion (the hydroxyl ion splits the proton from the α-carbon atom):



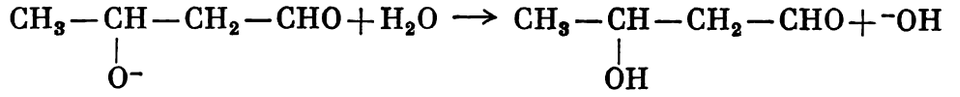
Carbanion

The carbanion formed is a nucleophile. It interacts with the carbonyl group of another molecule of a carbonyl compound according to the general scheme of reactions with nucleophilic reagents:



Alkoxide ion

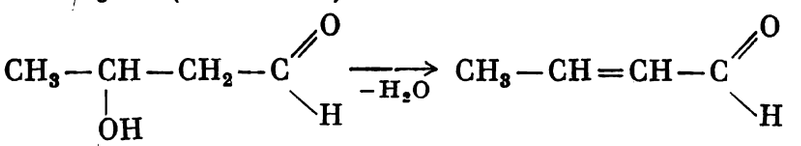
The alkoxide ion abstracts a proton from water, forming β-hydroxy aldehyde and regenerating the hydroxyl anion:



Aldol (3-hydroxybutanal)

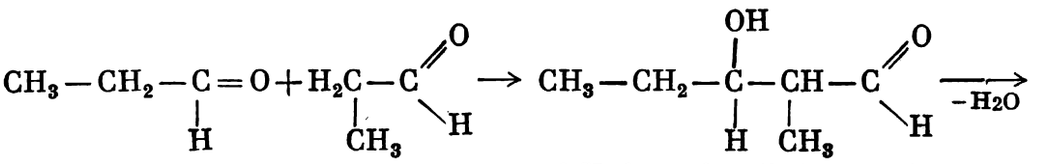
The condensation product of two molecules of acetaldehyde is known as *aldol* (an abbreviation of the words "*ald*ehyde alco*hol*"), and this indicates the presence of two functional groups, the aldehyde and the alcoholic groups, in the molecule. This reaction is known as *aldol condensation.* This condensation does not occur if aldehyde has no α-hydrogen, e.g., $(CH_3)_3C—CHO$ and Ar—CHO.

When aldol is heated, it is capable of losing water and turning into *crotonaldehyde* (2-butenal):

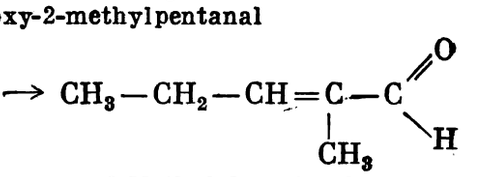


The condensation reaction with the elimination of water and the formation of an unsaturated carbonyl compound is known as *croton condensation.*

Like acetaldehyde, its homologues are also condensed, and always at the expense of α-hydrogen atoms:



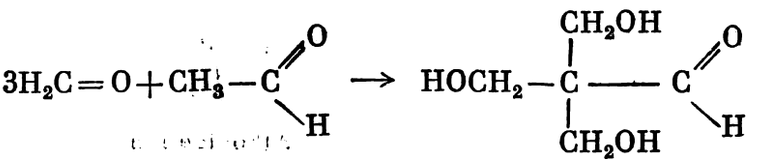
3-Hydroxy-2-methylpentanal



2-Methyl-2-pentenal

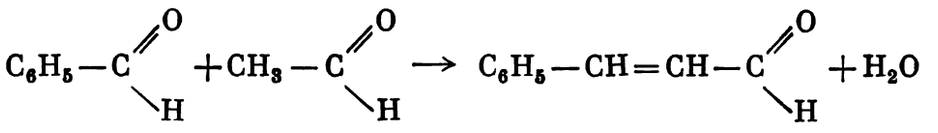
The compounds formed contain a double carbon-carbon bond in *conjugation* with the double carbon-oxygen bond, and they are especially advantageous energetically. This explains why such a reaction occurs readily.

Molecules of different aldehydes can also enter into the reaction. For example, formaldehyde is characterized by condensation with other aldehydes which results in the formation of polyhydric aldehyde alcohols:



This reaction occurs under the action of alkali carbonates (K_2CO_3, Na_2CO_3).

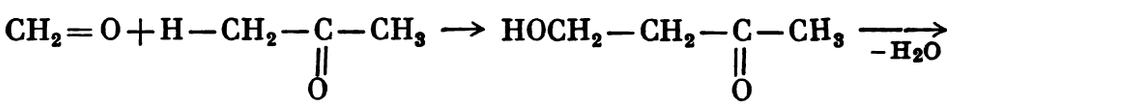
Aromatic aldehydes, which contain the aldehyde group in the nucleus, cannot be condensed between themselves owing to the absence of α-hydrogen. They undergo croton condensation with aliphatic aldehydes, which contain α-hydrogen:



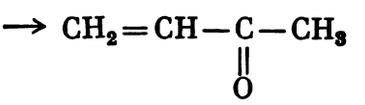
Cinnamaldehyde

There are many related reactions in which the carbanionic particle is formed not from aldehydes and ketones, but from other compounds (see, for instance, p. 313).

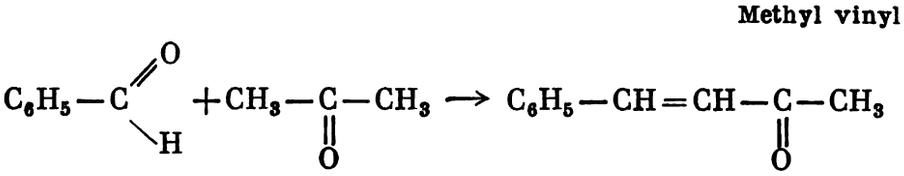
2. Condensation between aldehydes and ketones. In this reaction, ketones act as a methylene component, because the carbonyl group of ketones is less active than that of aldehydes:



4-Hydroxy-2-butanone

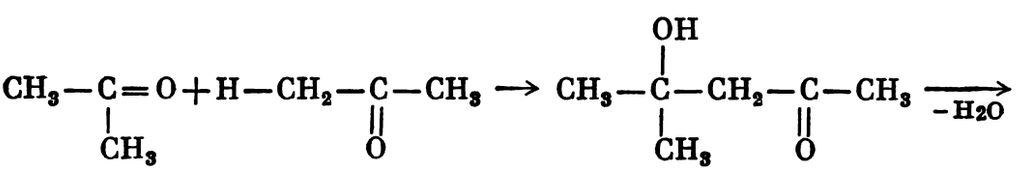


Methyl vinyl ketone

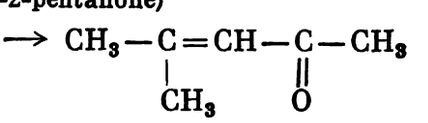


Benzalacetone

3. Condensation between ketones. The most active ketones are capable of being condensed like aldehydes:



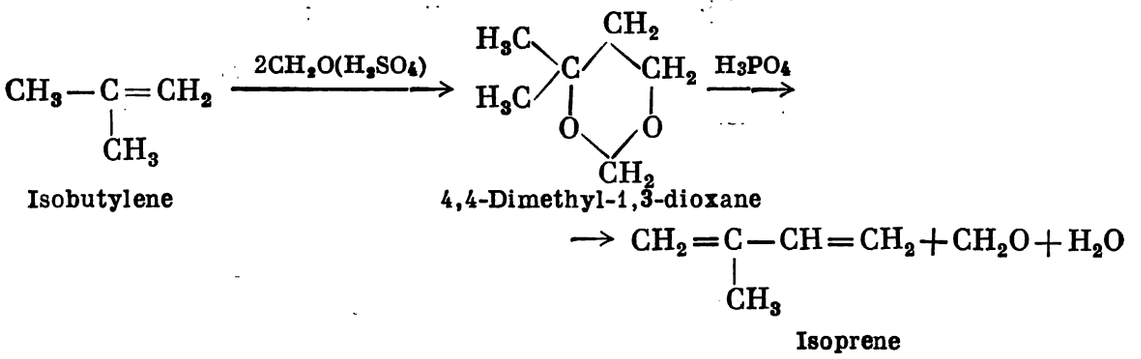
Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)



Mesityl oxide (4-methyl-3-penten-2-one)

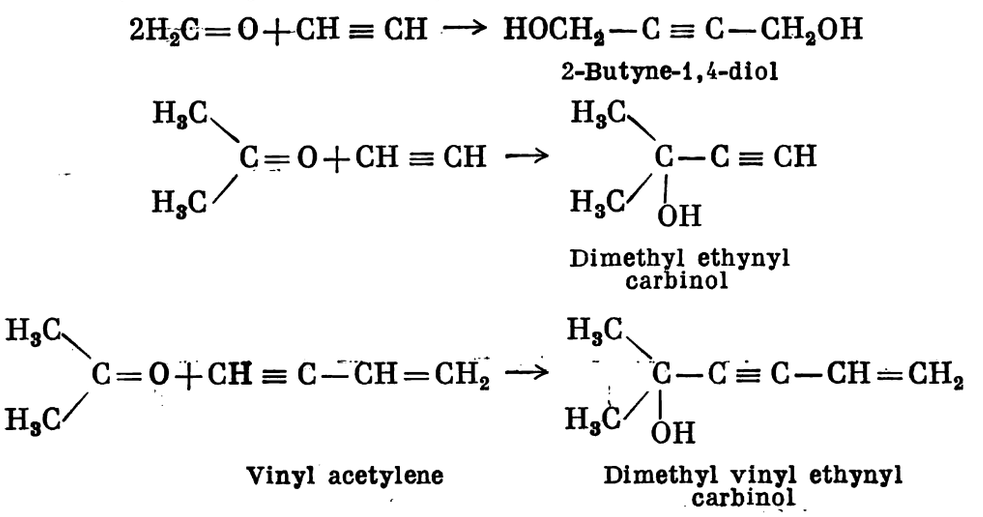
4. Condensation of aldehydes and ketones with hydrocarbons.

(a) Condensation with alkenes. 4,4-Dimethyl-1,3-dioxane is formed when excess formaldehyde interacts with isobutylene in the presence of sulphuric acid. It is an interesting substance, because an important industrial product, *isoprene*, can be obtained from it under the action of phosphoric acid (200°C):



Isobutylene — 4,4-Dimethyl-1,3-dioxane — Isoprene

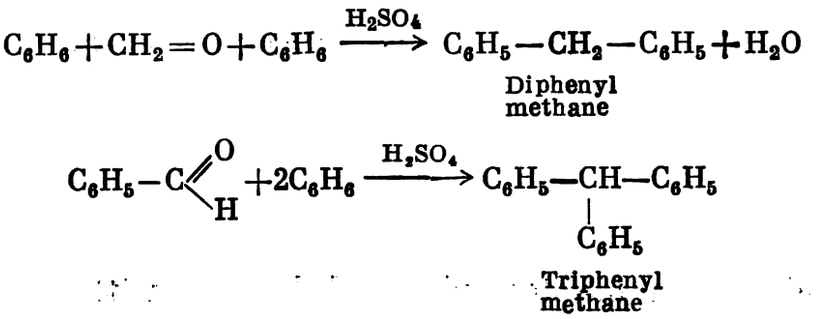
(b) Condensation with acetylene and 1-alkynes. The reaction occurs in the presence of powdery caustic alkalies or alkali-metal alkoxides (*Favorsky's reaction*):



2-Butyne-1,4-diol — Dimethyl ethynyl carbinol — Vinyl acetylene — Dimethyl vinyl ethynyl carbinol

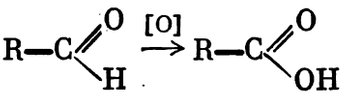
The acetylenic alcohols obtained by these reactions serve as starting substances in different syntheses.

(c) Condensation with aromatic hydrocarbons. When aromatic hydrocarbons are condensed with aldehydes, they yield compounds of the diphenyl and triphenyl methane series:

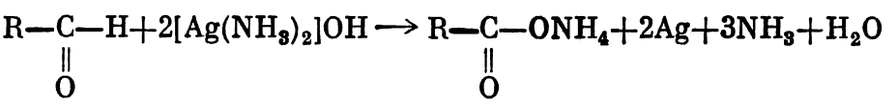


Diphenyl methane — Triphenyl methane

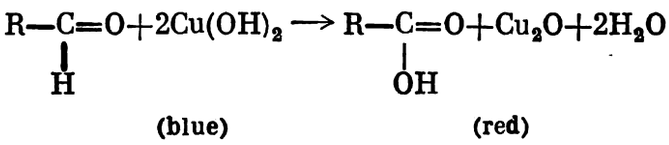
Oxidation of aldehydes and ketones. Aldehydes and ketones behave differently towards the action of oxidizing agents. The presence of hydrogen in the aldehyde group facilitates its oxidation to the carboxyl group, as a result of which acids having the same number of carbon atoms in a molecule are formed:



Aldehydes are oxidized by weak oxidizing agents, e.g., by an ammoniacal solution of silver nitrate, which contains the complex compound $[Ag(NH_3)_2]OH$. In this case, a layer of metallic silver, a mirror, is deposited on the surface of a glass vessel:

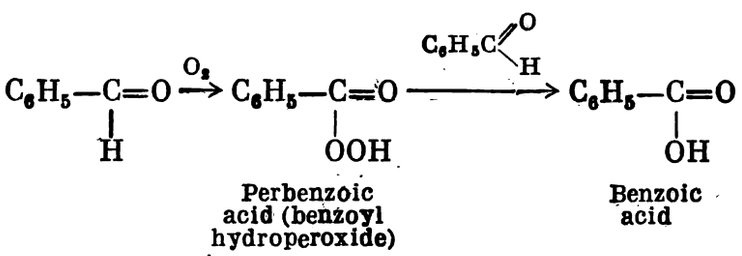


This reaction and also the reducing of the Fehling solution or freshly-precipitated cupric hydroxide are used to identify aldehydes:



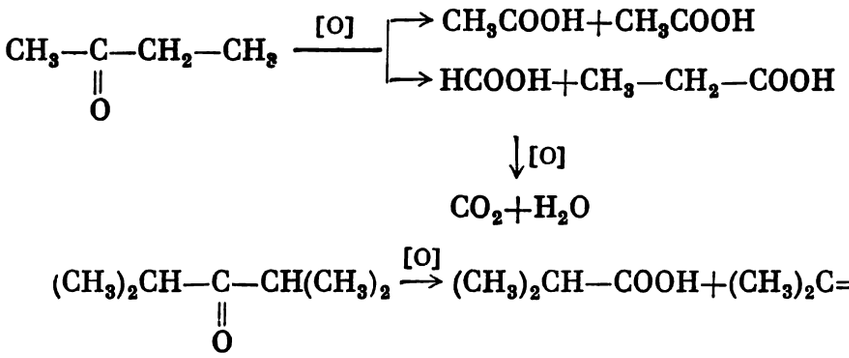
Ketones do not give these reactions.

Many aldehydes are readily oxidized by atmospheric oxygen. Peroxide compounds, peracids, are formed as intermediate products. The oxidation of benzaldehyde has been studied best of all:

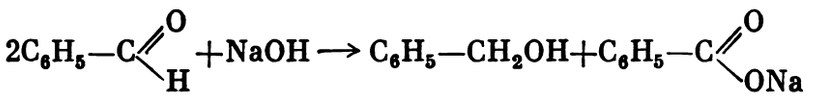


Ketones are oxidized with considerably greater difficulty, and they are stable with respect to weak oxidizing agents and atmospheric oxygen. The action of strong oxidizing agents on ketones under drastic conditions causes the rupture of the carbon-carbon bond, and this results in the formation of a mixture of different products (acids and ketones) having less carbon atoms than the initial ketone. The structure of the initial ketone can be determined from oxidation

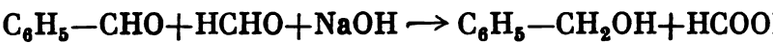
products:



Aromatic aldehydes which have no α-hydrogen in the molecule are characterized by the *Cannizzaro reaction* (1853), i.e., the oxidation of one molecule at the expense of another under the action of concentrated alkalies (one aldehyde molecule is oxidized to acid, while another is reduced to alcohol):

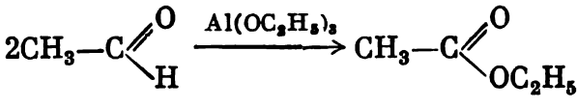


A mixture of higher aldehyde and formaldehyde participates in crossed Cannizzaro reaction, which has been studied by V. M. Rodionov:

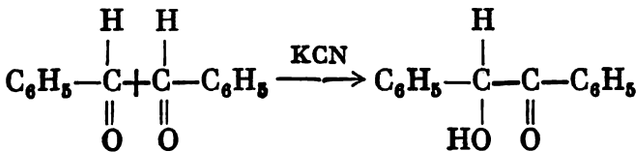


In this reaction, aromatic aldehyde is reduced, while formaldehyde is oxidized.

Aliphatic aldehydes containing α-hydrogen behave differently under the action of alkalies: they at first condense into aldols, and then high-molecular-weight compounds are formed from them. But the oxidation-reduction transformation, like the one considered above, can occur under the action of aluminium ethoxide (*Tishchenko's reaction*, 1906). In this case, esters are formed:



Benzaldehyde is characterized by *benzoin condensation* (N. N. Zinin, 1839): it yields *benzoin* under the action of potassium cyanide:



Benzoin

Other reactions. As we have already seen in our consideration of condensation reactions, the carbonyl group increases the mobility of α-hydrogen atoms in the molecule. For example, α-hydrogen is

readily replaced by a halogen (chlorine, bromine, iodine):

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3+Cl_2 \longrightarrow ClCH_2-\underset{\underset{O}{\|}}{C}-CH_3+HCl$$

Chloroacetone

In the compounds obtained, a halogen in the α-position is also characterized by great activity.

It has been noted that the chemical properties of aldehydes and ketones are similar due to the presence of a carbonyl group in the molecules of these compounds. But they also differ from one another, especially as regards their behaviour towards oxidizing agents. Aldehydes alone produce a colour reaction with fuchsin sulphurous acid. The polymerization reaction is characteristic of aldehydes.

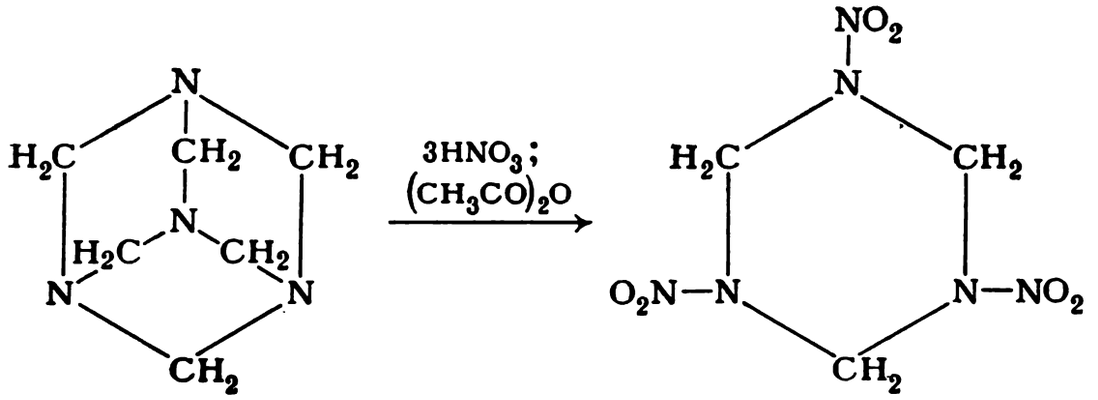
11.5. Important Individual Aldehydes and Ketones. *Formaldehyde* (*methanal*) is a gas which has a pungent irritating odour. It is formed when many organic substances partially burn up. Traces of formaldehyde are always contained in smoke, and this explains why it has a preserving effect when meat and fish products are being smoked.

Formaldehyde is obtained industrially from methanol by passing alcohol vapours together with air over a heated copper (or silver) catalyst. The method of partially oxidizing methane is of less importance. Formaldehyde is preserved as a 40 per cent aqueous solution called *Formalin* or as solid compounds called *trioxane* $(CH_2O)_3$ and *paraformaldehyde* $(CH_2O)_n$.

The absence of an organic radical in the molecule of formaldehyde affects its chemical properties. For example, unlike other aldehydes, formaldehyde with ammonia yields a cyclic compound known as *hexamethylenetetramine* (*urotropine*):

$$6CH_2O+4NH_3 \longrightarrow C_6H_{12}N_4+6H_2O$$

The reaction was discovered by A. M. Butlerov (1860). Urotropine is a crystalline substance having a melting point of 230°C. It is employed as a medicinal and used in large amounts for producing polymers. *Hexogen*, a strong explosive, is obtained when nitric acid acts on urotropine:



Hexamethylenetetramine Hexogen

Formaldehyde is characterized also by the Cannizzaro reaction (Sec. 11.4):

$$2HCH{=}O \longrightarrow CH_3OH + HCOONa$$

Formaldehyde enters into a condensation reaction of the aldol type under the action of calcium hydroxide:

$$H{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix} + H{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix} \longrightarrow HOCH_2{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix}$$

Glycolaldehyde

Glycolaldehyde then condenses into monosaccharide.

The reaction between formaldehyde and phenols is considered in Sec. 10.9.

Formaldehyde is widely used for different syntheses. It is toxic for microorganisms, and therefore it is employed as a disinfectant, e.g., for mordanting seeds before sowing them (smut spores are destroyed). Formaldehyde is used in the tanning industry, for preserving anatomical preparations, etc.

Acetaldehyde (*ethanal*) is a readily boiling liquid which has an odour of green leaves. It is obtained industrially from acetylene by Kucherov's reaction (see Sec. 5.4), and by ethyl alcohol oxidation and ethylene oxide isomerization (see Diagram 10.1). The modern industrial method is the catalytic oxidation of ethylene by atmospheric oxygen in the presence of a palladium catalyst ($PdCl_2$):

$$CH_2{=}CH_2 \xrightarrow{{}^1/_2O_2} CH_3{-}CHO$$

Acetaldehyde is used for obtaining acetic acid, ethyl acetate (condensation by Tishchenko's reaction), metaldehyde ("dry alcohol"), paraldehyde, and ethyl alcohol.

Chloral is obtained when excess chlorine acts on acetaldehyde:

$$CH_3{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix} + 3Cl_2 \longrightarrow CCl_3{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix} + 3HCl$$

Chloral is a liquid having a boiling point of 98°C; it forms, with water, a stable hydrate known as *chloral hydrate* $CCl_3CH(OH)_2$ (see Sec. 11.4), which is a crystalline substance (m.p. 57°C). This is a rare example of the stability of *gem*-diols.

When an aqueous alkaline solution acts on chloral, the carbon-carbon bond is cleaved and chloroform is formed:

$$CCl_3{-}C\!\!<\!\!\begin{matrix}O\\H\end{matrix} + NaOH \longrightarrow CHCl_3 + HCOONa$$

This reaction is used industrially for obtaining chloroform from acetaldehyde or from ethyl alcohol. At first, alcohol is oxidized to

acetaldehyde under the action of calcium hypochlorite (bleaching powder); acetaldehyde is then chlorinated to chloral, while the alkaline medium of the reaction promotes its cleavage and the formation of chloroform.

Benzaldehyde is a colourless oily liquid having an odour of bitter almond. It occurs in nature as part of the glucoside, amygdalin (see Sec. 19.2).

Benzaldehyde is obtained industrially by chlorinating toluene to benzylidene chloride (benzal chloride) with subsequent hydrolysis:

$$C_6H_5-CH_3 \xrightarrow{Cl_2} C_6H_5-CHCl_2 \xrightarrow{H_2O} C_6H_5-C\begin{matrix}O\\ \diagdown H\end{matrix}$$

or by catalytically oxidizing toluene:

$$C_6H_5-CH_3 \xrightarrow[\text{agent}]{\text{oxidizing}} C_6H_5-C\begin{matrix}O\\ \diagdown H\end{matrix}$$

The specifics of the chemical properties of benzaldehyde, connected with the absence of α-hydrogen in its molecule, have already been dealt with when considering the chemical properties of aldehydes. The reaction between benzaldehyde and chlorine occurs also differently from that between benzaldehyde and aliphatic aldehydes, i.e., hydrogen of the aldehyde group is replaced:

$$C_6H_5-C\begin{matrix}O\\ \diagdown H\end{matrix} \xrightarrow[-HCl]{Cl_2} C_6H_5-C\begin{matrix}O\\ \diagdown Cl\end{matrix}$$

Benzoyl chloride

This reaction is used for industrially producing benzoyl chloride. Benzaldehyde, being an aromatic compound, also produces characteristic reactions of the benzene nucleus, e.g., it is nitrated. The aldehyde group is a *meta*-director.

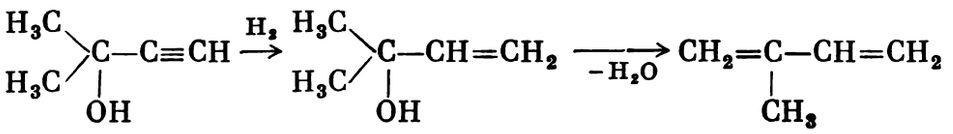
Benzaldehyde is used for synthesizing dyes, aromatic substances, etc.

Acetone is a liquid having a characteristic odour; it mixes with water in all proportions and is a good solvent of organic substances. It was formerly obtained industrially by subjecting calcium acetate to dry distillation (see Sec. 11.2). There are now also other methods of obtaining it: the catalytic ketonization of acetic acid, the acetone-butyl fermentation of saccharides, the dehydrogenation of isopropyl alcohol obtained from propylene, and the direct oxidation of propylene:

$$CH_2=CH-CH_3 \xrightarrow[(PdCl_2;\ Cu_2Cl_2)]{O_2} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

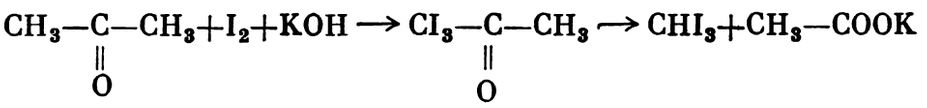
But the most important synthesis is the cumene method of obtaining phenol and acetone together (see Sec. 10.8).

Acetone is used as a solvent for lacquers, cinema films, cellulose acetate and acetylene, and as a gelating agent in the production of smokeless gunpowder. It is employed for synthesizing chloroform, iodoform, ketone, etc. The condensation product of acetone with acetylene, dimethyl ethynyl carbinol (see Sec. 11.4), is used for obtaining isoprene:



The condensation product of acetone with vinyl acetylene, dimethyl vinyl ethynyl carbinol (see Sec. 11.4), is used for obtaining vinyl acetylene polymers, glues (Nazarov's glue), lacquers, etc.

The qualitative reaction for acetone is the formation of iodoform when a solution of alkali and iodine acts on it:

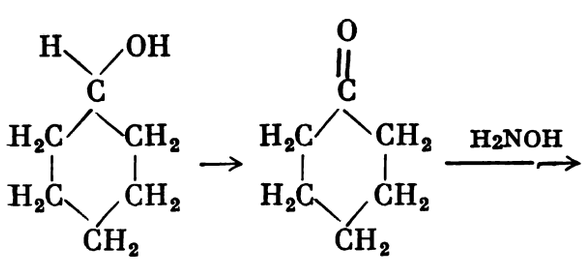


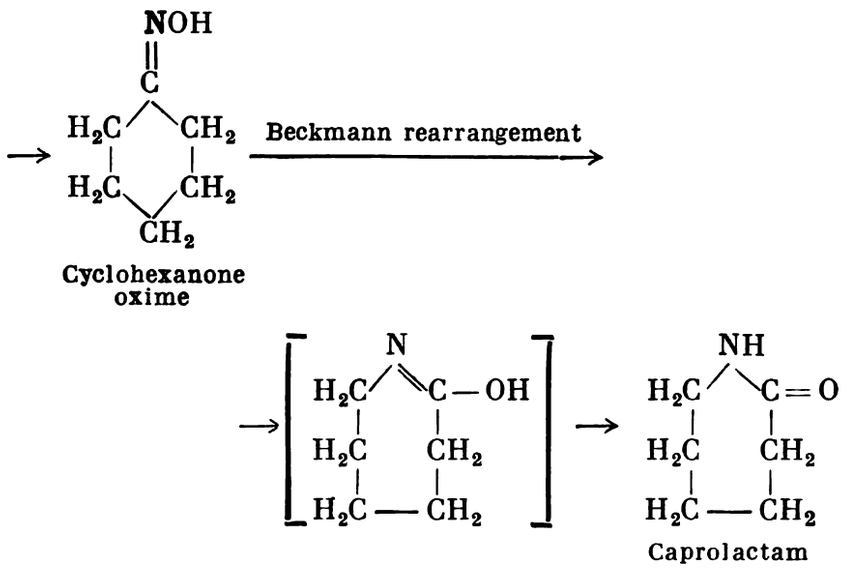
Iodoform is a crystalline substance which has a yellow colour and a peculiar odour.

This reaction is characteristic also of the acetone homologues—methyl ketones and, in general, of compounds whose molecule contains the grouping CH_3-C- or CH_3-CH-.

Cyclohexanone is a liquid having a b.p. of 166°C, it is obtained by dehydrogenating cyclohexanol or oxidizing cyclohexane.

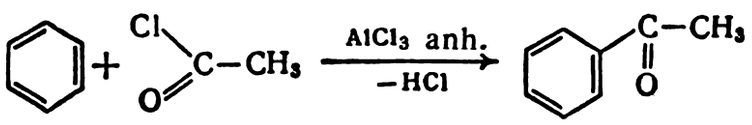
Cyclohexanone is used for producing caprolactam, which is the initial substance for obtaining the synthetic fibre called capron (nylon 6):



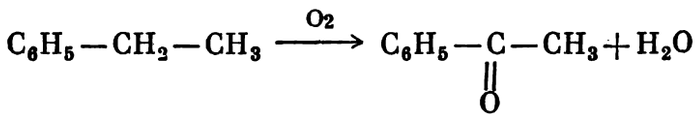


Adipic acid is formed when cyclohexanone is vigorously oxidized; the acid is used for manufacturing nylon.

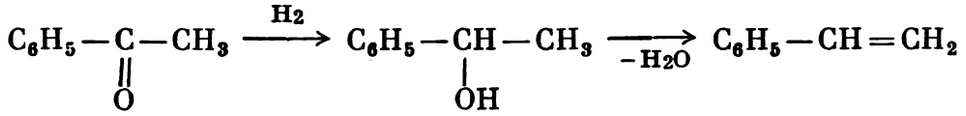
Acetophenone (*methyl phenyl ketone*) is a substance having a pleasant flowery odour, and therefore it is used for producing toilet soap. It is synthesized by the Friedel-Crafts reaction



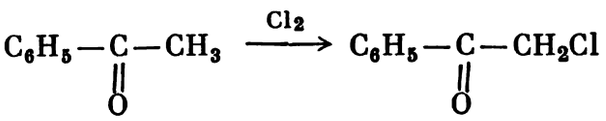
or by oxidizing ethylbenzene by atmospheric oxygen in the presence of catalysts:



Acetophenone is used in different syntheses. Its hydrogenation engenders methyl phenyl carbinol, from which styrene, an important industrial product, is obtained by dehydration:



When chlorine acts on acetophenone, *chloroacetophenone* is formed:

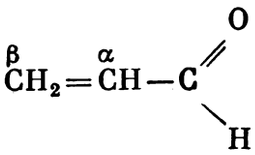


It is a crystalline substance having a m.p. of 52°C, it is a powerful lachrymator and was used as tear gas in World War I.

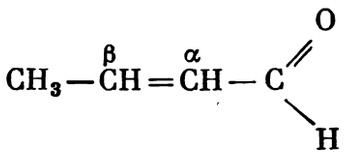
UNSATURATED CARBONYL COMPOUNDS

The presence of a carbonyl group and a double bond close to it in the molecule of a substance imparts special properties to a compound owing to the mutual effect of these groups. The most important groups are the conjugated systems C=C—C=O and the cumulated systems C=C=O. If a carbonyl group is remote from the double bond, each group retains its individuality and exhibits its inherent properties.

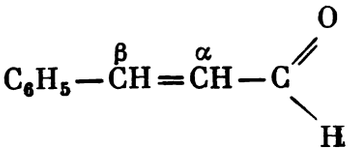
11.6. Conjugated or α,β-Unsaturated Aldehydes and Ketones. A general method of preparing them is by the croton condensation of aldehydes and ketones (Sec. 11.4). This method is used to obtain, for example, the following carbonyl compounds:



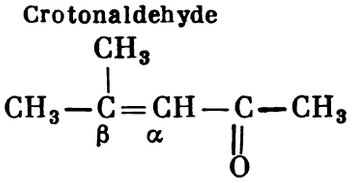
Acrolein



Crotonaldehyde



Cinnamaldehyde



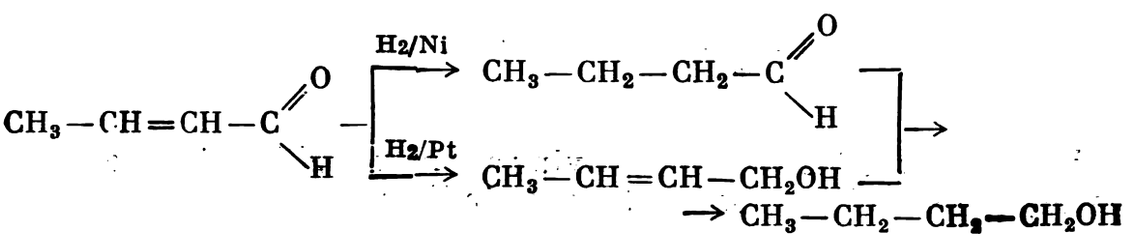
Mesityl oxide

A system of conjugated double bonds originates in the molecule when α,β-unsaturated carbonyl compounds are formed:

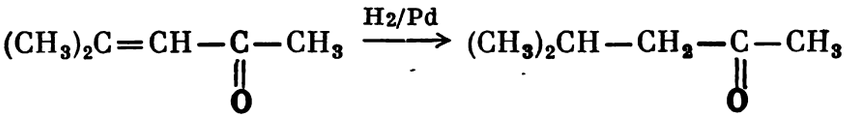
$$\overset{4}{C}=\overset{3}{C}-\overset{2}{C}=\overset{1}{O}$$

In addition reactions, such systems can react in the positions 1,2-, 3,4- and 1,4-, depending on the conditions and the reagent, i.e., only the carbonyl group or the double carbon-carbon bond, or both of them together participate in the reaction.

The double carbon-carbon bond of α,β-unsaturated compounds, unlike isolated double bonds, is highly active, and it can be hydrogenated by hydrogen not only in the presence of a catalyst, but also at the moment of isolation (by sodium amalgam in an aqueous alcoholic solution and by zinc in acetic acid). When α,β-unsaturated aldehydes are being hydrogenated, saturated aldehydes and unsaturated alcohols are formed; the end product of hydrogenation is saturated alcohols:

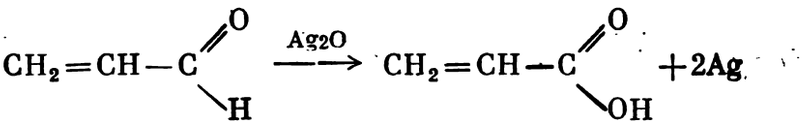


α,β-Unsaturated ketones are hydrogenated along the double carbon-carbon bond:

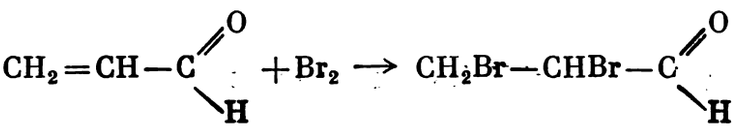


α,β-Unsaturated carbonyl compounds produce several typical reactions for the carbonyl group: they form cyanohydrins, oximes, hydrazones, etc.

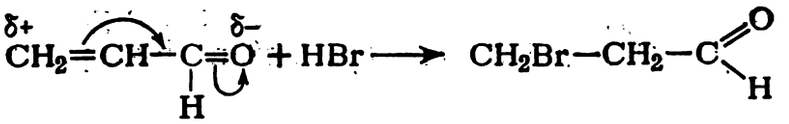
Oxidizing agents attack both the carbonyl group and the double bond, but only the carbonyl group is oxidized under the action of moist silver oxide:



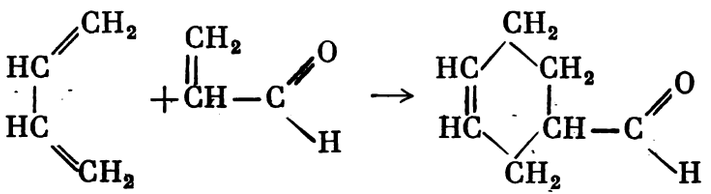
A halogen is added at the site of the C=C bond:



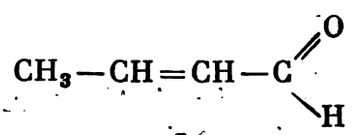
A hydrogen halide is added under the action of the carbonyl group *contrary to Markovnikov's rule*:



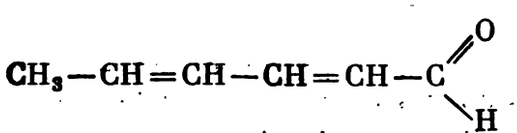
α,β-Unsaturated carbonyl compounds can be used as dienophiles in the Diels-Alder reactions:



The somewhat high activity of the α,β-double carbon-carbon bond is due to its conjugation with the carbonyl group $\overset{\beta}{C}=\overset{\alpha}{C}-C=O$. The transfer of the effect in the case of conjugation can extend also to several conjugated bonds. For example, croton I or sorbic II aldehydes

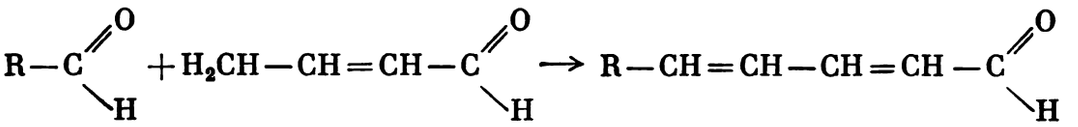


I



II

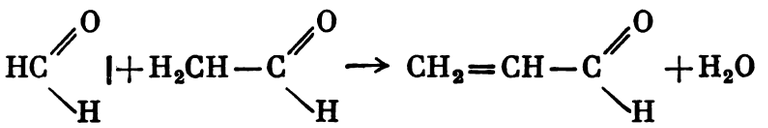
enter into the condensation reaction at the expense of hydrogen of the methyl group (like acetaldehyde):



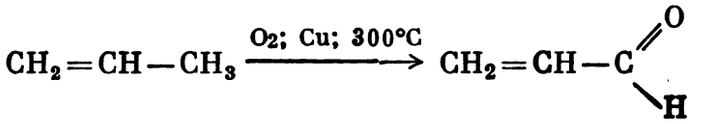
The similarity of the reactivity of the same groups in molecules, which differ from one another by a vinyl group —CH=CH—, has become known as *vinylogy*.

The following representatives of α,β-unsaturated aldehydes are of interest.

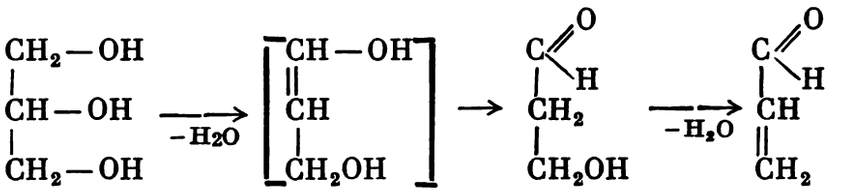
Acrolein, $CH_2=CH—CHO$, is a liquid having a pungent irritating odour and a b.p. of 52°C. It is obtained industrially by condensing formaldehyde with acetaldehyde



or by catalytically oxidizing propylene:



In the laboratory, acrolein is prepared from glycerol by heating it with dehydrating substances (potassium bisulphate, $KHSO_4$):



Acrolein is used for different syntheses and for obtaining transparent and hard plastics.

Crotonaldehyde is a liquid having a pungent suffocating odour and a b.p. of 102°C. It is obtained by the croton condensation of acetaldehyde.

When crotonaldehyde is being oxidized, crotonic acid $CH_3—CH=CH—COOH$ is readily formed, and its esters are used for producing polymeric materials. Butyraldehyde and 1-butanol are obtained when crotonaldehyde is hydrogenated.

11.7. Ketenes. They are compounds having a cumulated carbonyl bond and a double carbon-carbon bond.

Their simplest and most important representative is the compound $H_2C=C=O$, which is called *ketene* proper. It is obtained industrially

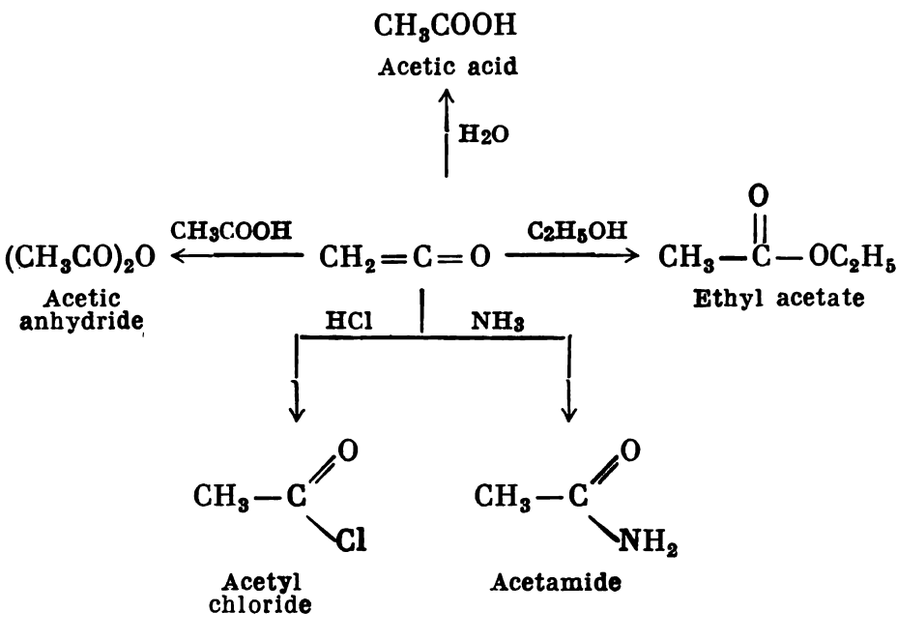
by dehydrating acetic acid in the presence of aluminium phosphate:

$$CH_3-COOH \xrightarrow[-H_2O]{700^\circ C} CH_2=C=O$$

In the laboratory ketene is obtained by pyrolysis of acetone:

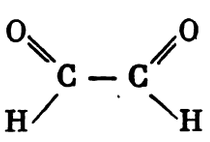
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{700^\circ C} CH_3-\overset{\overset{O}{\|}}{C}\cdot + CH_3\cdot \longrightarrow CH_2=C=O+CH_4$$

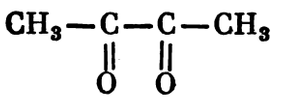
Ketene is a gas which liquefies at —41°C, and it is toxic. It is among the most reactive substances and is used as a good acetylating agent for different syntheses:

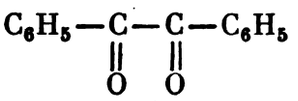


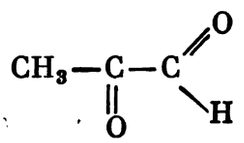
DICARBONYL COMPOUNDS. CHELATES

11.8. Properties and Individual Representatives. The simplest compounds which contain two neighbouring carbonyl groups (α-dicarbonyl compounds) are:

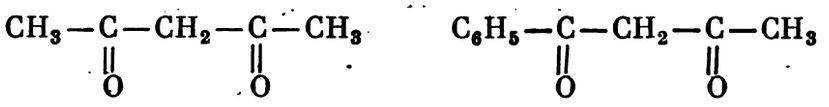

Glyoxal


Diacetyl (2,3-butanedione)


Benzil (dibenzoyl)

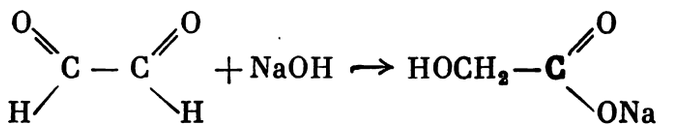

Methylglyoxal

The simplest representatives of β-dicarbonyl compounds containing carbonyl groups in the positions 1,3 are:

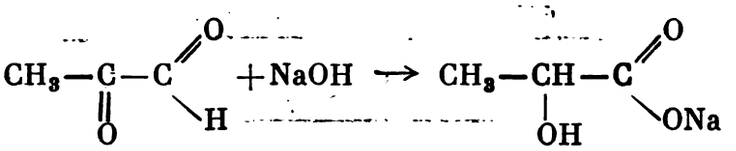


Acetylacetone Benzoylacetone

Carbonyl groups can be also in other positions in the molecule. The relative position of carbonyl groups affects the properties of compounds. Compounds containing carbonyl groups in the α-position are yellow owing to the conjugation of the π-bonds. They are highly active chemically and undergo Cannizzaro's intramolecular reaction in an alkaline solution:

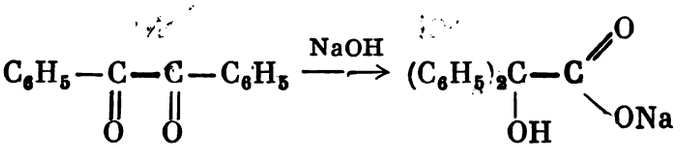


Glyoxal Sodium glycolate



Methylglyoxal Sodium lactate

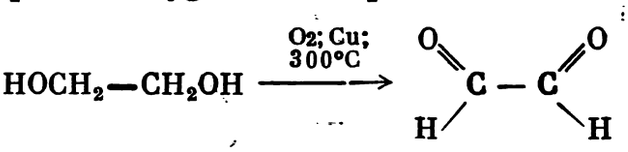
For aromatic α-diketones, such a reaction is known as the *benzilic acid rearrangement*:



Sodium benzilate

Let us consider the following representatives of dicarbonyl compounds.

Glyoxal, OHC—CHO, is a yellow substance which melts at 15°C and boils at 51°C. Glyoxal vapours are green. In an aqueous solution, it yields colourless hydrate $(HO)_2CH—CH(OH)_2$. When aqueous solutions are being evaporated, it readily polymerizes, forming colourless polymers. Glyoxal is obtained by oxidizing ethylene glycol by atmospheric oxygen in the presence of a copper catalyst:



Diacetyl (*dimethylglyoxal*), $CH_3—CO—CO—CH_3$, is a yellow liquid which boils at 88°C. It is obtained from methyl ethyl ketone under

the action of nitrous acid in the cold (α-hydrogen of the methylene group enters into the reaction) with the subsequent decomposition of monoxime:

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{HONO} CH_3-\underset{\underset{HON}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{H_2O(H^+)} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

Diacetyl dioxime, *dimethylglyoxime*, $CH_3-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$ (Chugaev's reagent), with nickel ions produces a characteristic pink precipitate. This reaction, discovered by L. A. Chugaev in 1906, is used in analytical chemistry for qualitatively and quantitatively determining nickel.

Compounds containing carbonyl groups in the β-position exhibit special properties.

It has already been noted that the carbonyl group activates α-hydrogen atoms and makes them more mobile. In β-dicarbonyl compounds, α-hydrogen atoms are between two carbonyl groups, and their mobility is even greater.

A representative of β-dicarbonyl compounds is *acetylacetone*, $CH_3-CO-CH_2-CO-CH_3$. It is a colourless liquid whose b.p. is 139°C, and d_4^{20}, 0.98. It is obtained by condensing ethyl acetate with acetone:

$$CH_3-\underset{\underset{O}{\|}}{\overset{OC_2H_5}{\overset{/}{C}}} + CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{C_2H_5ONa}$$

$$\rightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + C_2H_5OH$$

It has been ascertained that acetylacetone is an equilibrium mixture of molecules of two forms, i.e., acetylacetone (15 per cent) and *enol*, which is an unsaturated keto alcohol of the ethylene series that is isomeric relative to acetylacetone, having a hydroxyl attached to the double bond (85 per cent):

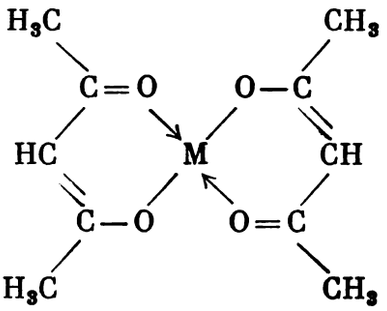
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftarrows CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$$

Keto form Enol form

This phenomenon, known as keto-enol tautomerism, is considered in greater detail in Sec. 18.9.

The acidic properties of the enol form of acetylacetone are more pronounced than those of alcohols, and therefore acetylacetone readily produces metallic derivatives, *enolates*, with bases.

Cations of polyvalent metals (copper, beryllium, aluminium, chromium, iron, etc.) with acetylacetone form stable enolates containing metal in the ring. These compounds are known as *chelates* (from the Greek word "chele", meaning "claw") or *chelate compounds*:



Metal acetylacetonate

See Sec. 14.1 for greater details on the nature of the bonds indicated by an arrow.

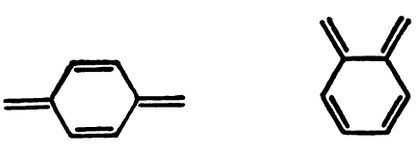
It has now been proven that the chelate ring in acetylacetonates exhibits aromatic properties and that all the bonds in it are equalized.

A characteristic chelating agent is the ion of bivalent copper. When acetylacetone is mixed together with freshly-precipitated cupric hydroxide, the latter at first passes into solution, and then sparingly soluble dark-blue copper acetylacetonate (whose structure is similar to that given above) is isolated. Chelates are almost insoluble in water, but they dissolve well in organic solvents. Many modern organic reagents used in analytical chemistry for detecting and quantitatively determining metal ions are substances which form chelates, such as nickel dimethylglyoximate.

Chelate compounds are now important also in obtaining high-purity metals.

QUINONES

11.9. Properties and Individual Representatives. Dihydric phenols having hydroxyl groups in the *ortho-* and *para*-positions are readily oxidized, forming cyclic diketones known as *quinones*. The bond structure characteristic of these compounds is known as a *quinoid* one:

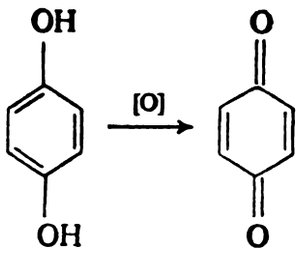


p-Quinoid structure

o-Quinoid structure

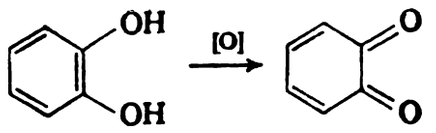
The quinoid ring is not aromatic. It is a cyclic conjugated system, and therefore quinones exhibit the properties of unsaturated compounds and ketones.

When hydroquinone is oxidized, *p*-benzoquinone is obtained



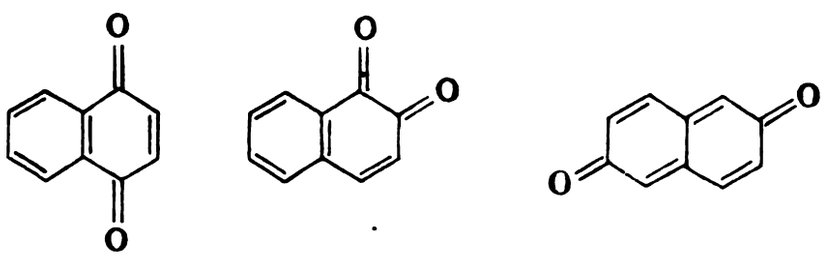
Hydroquinone — *p*-Benzoquinone

and when pyrocatechin (catechol) is oxidized, *o*-benzoquinone can be obtained:



Pyrocatechin — *o*-Benzoquinone

Naphthoquinones are formed when naphthalene is oxidized by a chromic-acid mixture or, even better, by 1,4-, 1,2- and 2,6-dihydroxynaphthalenes or the corresponding aminonaphthols:

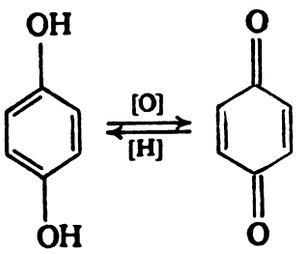


p-Naphthoquinone *o*-Naphthoquinone *amphi*-Naphthoquinone

The quinoid structure is possessed by many synthetic dyes, and it is found also in many complex natural organic compounds.

p-Benzoquinone was obtained by A. A. Voskresensky from quinic acid (1838), and hence its name *quinone*. It is a light-yellow crystalline substance having a penetrating odour, and its vapours have an irritating effect on the mucous membrane.

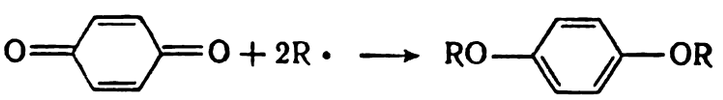
Hydroquinone and quinone are bound by a mutual transformation. Their interconversion is an oxidation-reduction reaction:



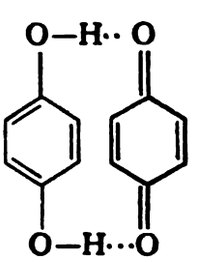
Hydroquinone Quinone

The reduction of quinone is used for industrially producing hydroquinone, while quinone is obtained by oxidizing aniline, $C_6H_5NH_2$.

Quinone is a good stabilizer of monomers in storage. It readily reacts with free radicals, binding them and terminating the growth of a polymer chain:

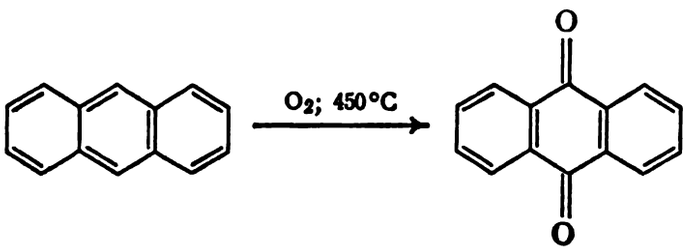


It is used as an inhibitor of the free-radical polymerization process. When alcohol solutions of equal amounts of quinone and hydroquinone are mixed together, a molecular compound known as *quinhydrone* (dark-green crystals) is formed:

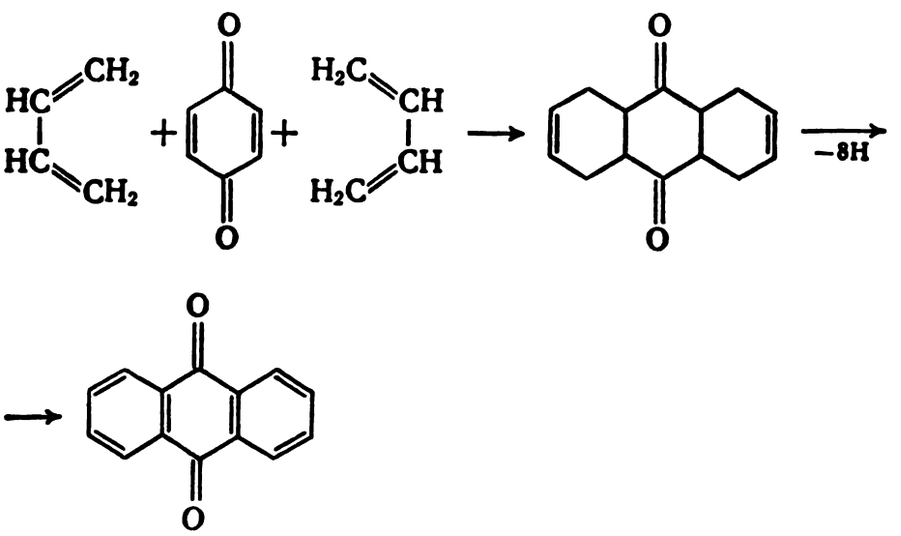


Anthraquinone is light-yellow crystals which melt at 286°C. It is obtained industrially by oxidizing anthracene over a vanadium

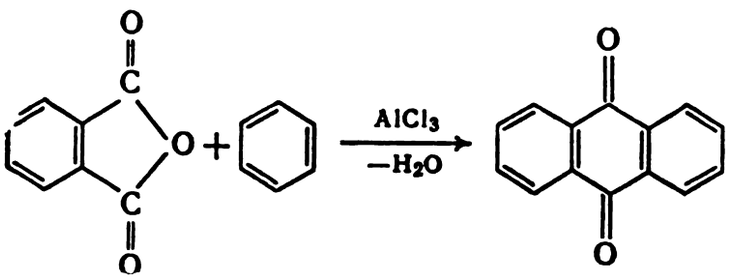
catalyst (V_2O_5)



or by means of diene synthesis from butadiene and quinone (quinones are good dienophiles, because their double bond is in conjugation with a carbonyl group)



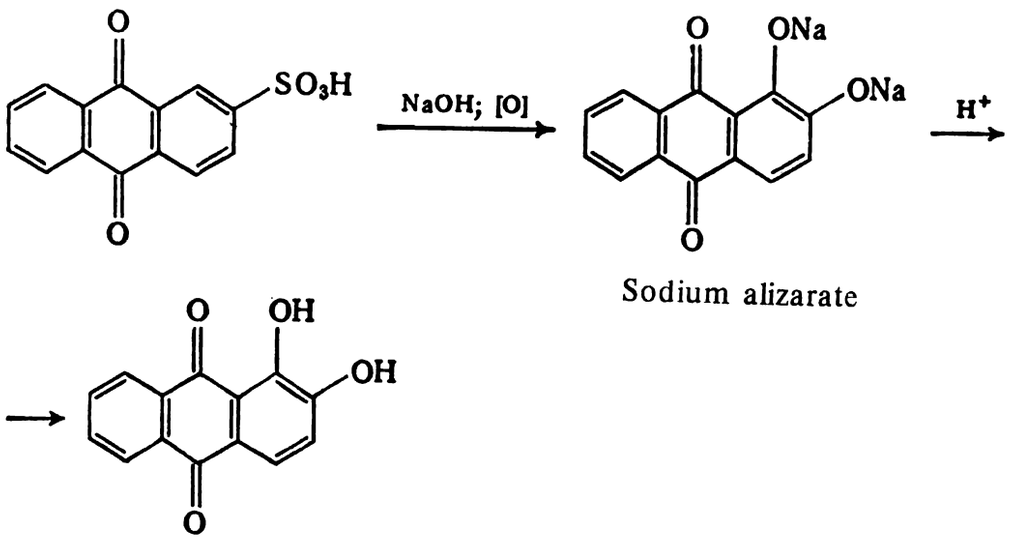
or by condensing benzene with phthalic anhydride (see Sec. 12.16):



Anthraquinone is used industrially for synthesizing dyes, such as alizarin.

The dye *alizarin* has been known from hoary antiquity. It is 1,2-*dihydroxyanthraquinone*. Alizarin was formerly obtained from madder roots. It was synthesized for the first time in 1868 by Graebe and Liebermann from anthraquinone. This method with slight modifications is used even now. It consists in the simultaneous action of alkali and an oxidizing agent (air or sodium chlorate) on

anthraquinone-β-sulphonic acid:



Sodium alizarate

Alizarin

Alizarin is a typical mordant dye.

Mordant dyeing is a process in which textiles are at first impregnated with mordants (salts of weak acids and weak bases, tannin, etc.), and then with dyes. When such a textile is treated with water vapour, mordants with alizarin produce stable compounds of the chelate type. The dye colour can change under the action of a mordant.

At present, other dyes which excel alizarin by quality and brilliance of colour are also obtained from anthraquinone.

Chapter 12

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Carboxylic acids are compounds whose molecule contains the functional group $-C\overset{O}{\underset{OH}{<}}$, usually written as —COOH. It is called the *carboxyl* group and is a combination of a carbonyl $>C=O$ and a hydroxyl —OH group.

Carboxylic acids can be regarded as hydrocarbon derivatives in which the hydrogen atom is replaced by the carboxyl group R—COOH.

Hydrogen in the carboxyl group is acidic. There are *monobasic* (monocarboxylic), *dibasic* (dicarboxylic) and *polybasic* (polycarboxylic) acids, depending on the number of carboxyl groups. Acids can be saturated, unsaturated, aromatic, and so forth, in conformity with the nature of the radical attached to the carboxyl group.

MONOBASIC CARBOXYLIC ACIDS

12.1. Isomerism. Nomenclature. The general formula of the homologous series of saturated monobasic acids is $C_nH_{2n+1}COOH$, or $C_nH_{2n}O_2$.

Monobasic acids having the alkyl or the alkenyl radical are known as *fatty acids* from their occurrence in natural vegetable and animal fats and oils in the form of esters.

The **isomerism** of monobasic acids, like that of aldehydes, is engendered by the radical structure.

Nomenclature. For the lower members of the carboxylic acid series, *trivial names* are most commonly used: formic, acetic, propionic and butyric acids, etc.

The prefix **iso** is used in the names of branched acids containing, in the branch, the methyl group at the chain end as it extends away from the carboxyl, i.e., at the second last carbon atom [i.e., they have the grouping $\left[\begin{matrix}H_3C\\ \\ H_3C\end{matrix}\!\!>\!CH-\right]$.

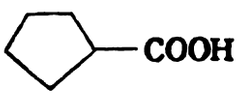
In *rational nomenclature*, use is made of the name in which complex acid is regarded as a derivative of acetic or other less complex acid.

By modern international rules, the name of a carboxylic acid is composed by adding the suffix **oic** and the word "acid" to the name of a hydrocarbon. The carbon atom of the carboxyl group is given the number 1 (see Table 12.1).

TABLE 12.1. **Some Carboxylic Acids**

Formula	Name	
	trivial	in modern international nomenclature
$H-COOH$	Formic	Methanoic
CH_3-COOH	Acetic	Ethanoic
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-COOH$	Isobutyric, dimethylacetic	2-Methylpropanoic
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-COOH$	Isovaleric, isopropylacetic	3-Methylbutanoic
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH-CH_2-COOH$	—	5-Methyl-3-hexenoic

In many cases, acids are termed also in accordance with the *carboxylic* system. An acid is regarded as a product of replacement of hydrogen by the carboxyl group. For example, acetic acid is called methanecarboxylic acid; propionic acid, ethanecarboxylic acid, and cyclic acid having a five-membered cyclic radical, cyclopentane carboxylic acid:



The *acid radical* or *acyl* is a univalent residue $R-\overset{\displaystyle O}{\overset{\Vert}{C}}-$, which is formed from the acid molecule as the hydroxyl group moves away. The names of acyls are derived from the Latin names of acids:

$H-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	$CH_3-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	$CH_3-CH_2-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	$C_6H_5-\overset{\displaystyle O}{\overset{\Vert}{C}}-$
Formyl	Acetyl	Propionyl	Benzoyl

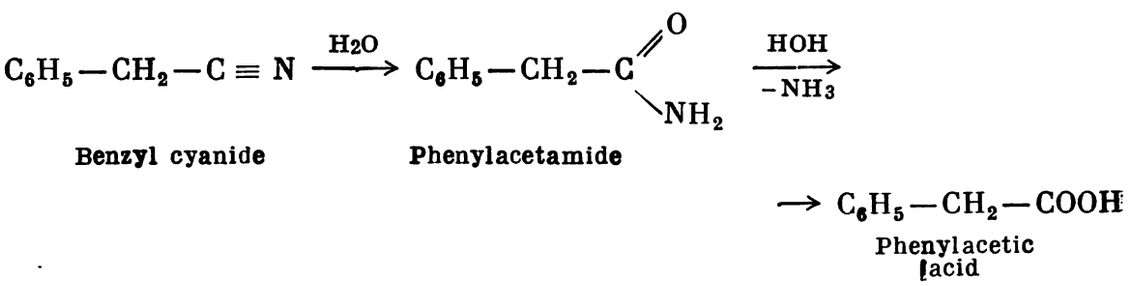
The names of salts are derived from those of acyls by replacing the suffix **yl** with **ate**. For example, the salts of the acids corresponding to the given acyls are called formate, acetate, propionate and benzoate.

12.2. General Preparation Methods. 1. Methods based on oxidation. Acids are formed when some organic substances are oxidized. We have already become acquainted with many reactions of this type. When alkenes are oxidized by strong oxidizing agents ($KMnO_4$, CrO_3), the molecule is ruptured at the site of the double bond. The oxidation of primary alcohols and aldehydes produces acids with the same number of carbon atoms, while in ketone oxidation, acids having less carbon atoms in the molecule than initial ketone are obtained (see Secs. 10.4 and 11.4).

Acids of the aromatic series are obtained by oxidizing benzene homologues: the carbon atom of the side chain linked with the benzene nucleus is oxidized to a carboxyl (see Sec. 7.5).

The oxidation of higher petroleum alkanes is of great practical importance in obtaining higher fatty acids. The starting raw material is paraffin (a mixture of higher alkanes). To this end, air is passed through molten paraffin at 100°C in the presence of manganese salts as catalysts. In this case, alkane molecules are split up and a mixture of acids is formed.

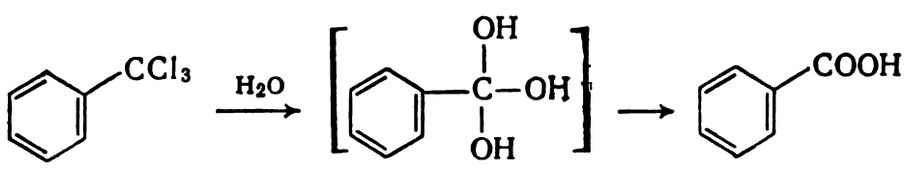
2. Methods based on hydrolysis. The saponification of nitriles in the acid or the alkaline medium at first gives acid amides, which are then hydrolyzed to acids:



Benzyl cyanide — Phenylacetamide — Phenylacetic acid

This method makes it possible to obtain acids containing one carbon atom more than the parent alkylhalide (see Sec. 9.4).

The hydrolysis of trihalogen derivatives, which contain three halogen atoms attached to one carbon atom, also produces acids:



Benzotrichloride — Benzoic acid

Higher acids having a normal carbon atom chain are extremely widely distributed naturally as fats, which are esters. In fat hydrolysis, fatty acids or their salts are obtained (see Sec. 12.22).

3. Carboxylation of organometallic compounds (see Sec. 17.2).

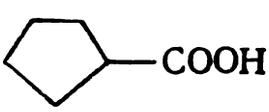
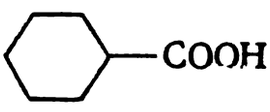
4. The alkene carbonylation method. Acids can be obtained from petroleum cracking products when carbon monoxide and water act on alkenes on heating under pressure in the presence of a nickel catalyst:

$$CH_2=CH_2 \xrightarrow[300^\circ C;\ 150\ kg/cm^2]{CO+H_2O} CH_3-CH_2-COOH$$

There are many other methods of synthesizing acids.

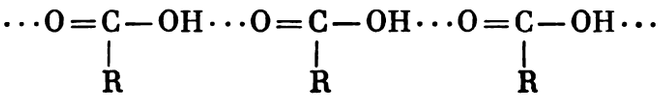
12.3. Physical Properties. As Table 12.2 shows, acids have abnormally high boiling and melting points (even in comparison with alcohols). This is because they are characterized by considerably

TABLE 12.2. **Physical Properties of Some Monobasic Carboxylic Acids**

Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}	Dissociation constant in water at 25°C, $K_a \cdot 10^{-5}$
Formic	H—COOH	+8.4	100.7	1.22	17.7
Acetic	CH_3—COOH	+16.6	118.1	1.049	1.75
Propionic	C_2H_5—COOH	—22.0	141.1	0.99 (at 15°C)	1.3
Butyric	C_3H_7—COOH	—7.9	163.5	0.96	1.5
Isobutyric	$CH_3-CH(CH_3)-COOH$	—47.0	154.5	0.95	1.4
Valeric	C_4H_9—COOH	—34.5	187.0	0.94	1.4
Caproic	C_5H_{11}—COOH	—3.9	205.8	0.92	1.32
Enanthic	C_6H_{13}—COOH	—7.5	223.5	0.918	1.28
Palmitic	$C_{15}H_{31}$—COOH	+64.0	390 (decom.)	0.84 (at 80°C)	—
Stearic	$C_{17}H_{35}$—COOH	69.4	360 (decom.)	0.84 (at 80°C)	—
Cyclopentane carboxylic		—4	215	1.05	—
Cyclohexane carboxylic		+31	232	1.03 (at 34°C)	—
Benzoic	C_6H_5—COOH	122.0	249.0	—	6.5
Phenylacetic	$C_6H_5CH_2$—COOH	76.7	265	—	5.6

great association, which is caused by the hydrogen bonding. Such bonds are formed in acids owing to the interaction between hydroxyl hydrogen of one molecule and carbonyl oxygen of another.

Hydrogen bonds in acids are stronger than those in alcohols, because the O—H bond is polarized more in acid molecules. The association of molecules can be linear



but cyclic, or dimeric, association is more characteristic of them. In such dimers, the internuclear distance between two oxygen atoms

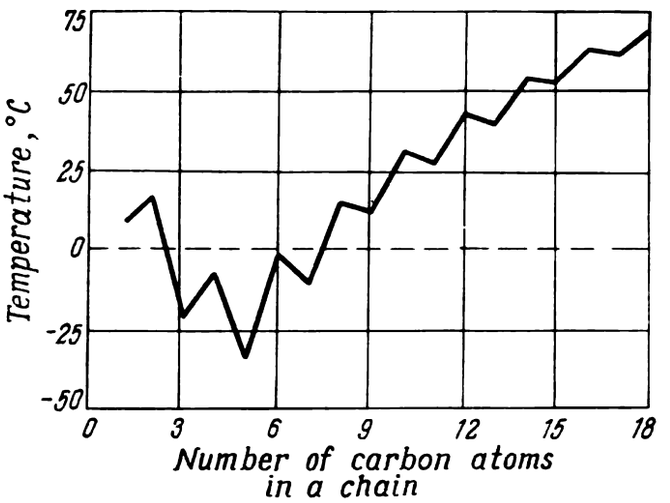
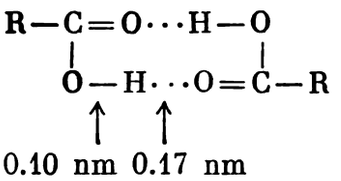


Fig. 12.1. Melting points of carboxylic acids

is 0.27 nm (like in associated alcohols), and the hydrogen atoms are remote from oxygen atoms at different distances:



Acetic acid is associated as dimers not only in the solid and liquid states, but also even in the gaseous state, and in hydrocarbon solutions. Dimers decompose into monomers only at high temperature.

The given table also shows that the boiling points rise smoothly as the hydrocarbon radical grows. In general, melting points also rise, but peculiar alteration is observed: each acid having an even number of carbon atoms in the molecule melts at a higher temperature than two of its neighbours having an odd number of carbon atoms (Fig. 12.1). The boiling points of acids with a normal chain are higher than those of their isomers with a branched chain. Acid density decreases as the hydrocarbon radical increases. The density of cyclic acids is greater than that of acyclic ones.

Lower acids have an acrid acidic odour, and the middle ones (C_4-C_8), an unpleasant rancid odour. Higher fatty (C_8 and higher) and aromatic acids have no odour.

Lower acids are well-soluble in water. Their water-solubility decreases as the hydrocarbon residue increases. The hydrocarbon residue is hydrophobic (it repulses water, like hydrocarbons). Acids are practically water-insoluble from C_9 and higher. But all acids dissolve in aqueous alkaline solutions, forming salts. Higher acids, like hydrocarbons, are well-soluble in ether and benzene.

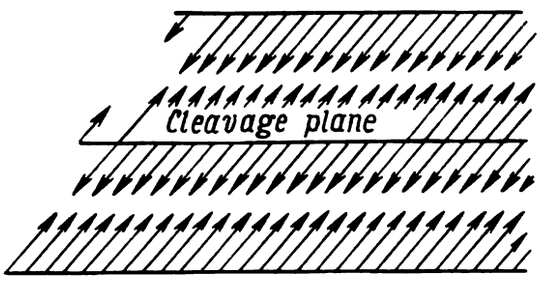
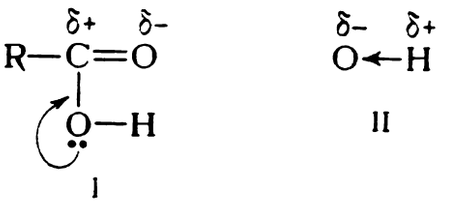


Fig. 12.2. Orientation of molecules in fatty acid crystals

Crystals of higher fatty acids (e.g., stearic acid) are slippery (they are oily to the touch). This is because molecules in crystals are arranged in parallel rows with carboxyl groups, which are turned towards one another (Fig. 12.2). The plane on which methyl groups are arranged is known as the *cleavage plane* of crystals. The bond between methyl groups is less strong than that between carboxyl groups, and slippage occurs on this plane.

12.4. Chemical Properties. The carboxyl group is a combination of two groups: the carbonyl group C=O and the hydroxyl group OH. These groups strongly affect one another owing to their close arrangement, and the properties of the carboxyl group are not a simple sum of those of the carbonyl and hydroxyl groups. The carboxyl group is a new functional group with its inherent properties. Carboxylic acids differ by their properties from aldehydes and ketones, and also from alcohols.

The hydroxyl group of acids eliminates a proton more readily than that of alcohols. Acidity increases owing to the effect of the polar carbonyl group. The carbonyl carbon atom, which is positively charged, tends to eliminate the shortage of electrons, attracting the electron pairs of not only the R—C and C=O bonds, but also the free electron pairs of hydroxyl oxygen. Therefore, hydroxyl oxygen draws away the electron pair of the O—H bond (I) more strongly, intensifying the positive charge on hydrogen (II):



Carboxylic acids are dissociated with the formation of the *carboxylate anion* and a proton:

$$R-\underset{\underset{O}{\|}}{C}-OH \rightleftarrows R-\underset{\underset{O}{\|}}{C}-O^- + H^+$$

There is equilibrium in an aqueous solution:

$$RCOOH + H_2O \rightleftarrows RCOO^- + H_3O^+$$

Hydroxonium ion

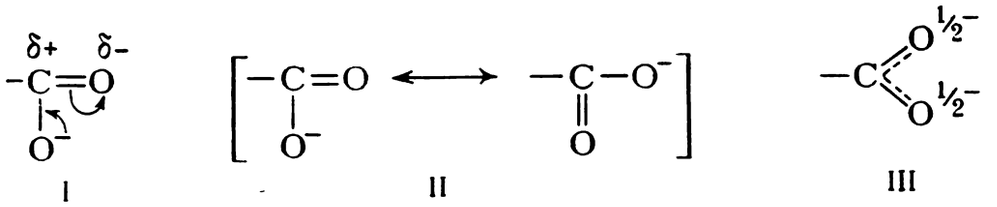
The equilibrium constant is the *acidity constant* K_a:

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

The quantity K_a is used for comparing the strength of acids (see Table 12.2).

Aqueous acidic solutions change the colour of indicators and are electrolytes. Although the acidic properties of carboxylic acids are more pronounced than those of alcohols and water, they are weak acids (except formic acid, which is of average strength) in comparison with strong mineral acids.

X-ray diffraction analysis has shown that both oxygen atoms in the carboxylate anion are equidistant from the carbon atom: the bonds are equalized when the anion is formed. The carboxylate anion is a typical example of mesomerism. Its structure can be expressed by several formulas: (I) by an indication of the electron shifts, (II) by a set of extreme formulas, and (III) by a formula with equalized bonds:



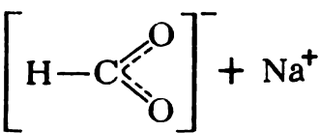
I II III

As we already know, the delocalization of electrons reduces energy. It follows that the formation of the carboxylate anion is energetically advantageous and is another reason why carboxylic acids are somewhat more acidic than alcohols. Formula III shows especially clearly that the bonds between carbon and oxygen are neither single nor double, but are equalized.

Thus, none of the carbon-oxygen bonds is of a carbonyl nature.

For sodium formate, in the carboxylate anion the length of the bond between the carbon atom and both oxygen atoms is the same,

being 0.127 nm; consequently, both oxygen atoms are equivalent:



The activity of the carbonyl group is determined by the quantity of the positive charge on the carbon atom, while in the carboxyl group, the positive charge of the carbon atom is extinguished to a considerable extent owing to conjugation with the free electron pairs of hydroxyl oxygen. The carbonyl group loses, under the action of the hydroxyl group, its tendency to react with nucleophilic reagents.

The carbon-oxygen bonds are not so equalized in the functional derivatives of acids as in the carboxylate anion. Therefore, such acid derivatives as esters RCOOR′ enter into some reactions characteristic of the carbonyl group.

The strength of acids, i.e., the readiness of proton elimination, is affected also by the radical which is attached to the carboxyl group. The dissociation constant values given in Table 12.2 show that formic acid is the strongest, while its homologues are weaker. This becomes clear if account is taken of the fact that alkyl groups, which have electron-donating properties, reduce the charge on the carbon atom of the carboxyl group and, consequently, its effect on the OH group.

The introduction of electron-accepting groups into the radical, especially in the α-position, intensifies acidic properties (see Sec. 18.1). The presence of a double bond in the α,β-positions considerably increases the strength of carboxylic acids and facilitates the formation of the carboxylate anion. Aromatic acids are stronger than aliphatic ones, e.g., benzoic acid C_6H_5—COOH is stronger than acetic acid.

The most typical reactions of acids are those connected with acidic properties, and reactions accompanied by a rupture of the oxygen-hydrogen bond, and those of substitution of the hydroxyl group.

The remaining part of the molecule may undergo reactions engendered by its structure: the presence of a multiple bond, the aromatic ring and other functional groups.

Let us consider the most important acid reactions:

1. Salt formation. Carboxylic acids readily react with bases, basic oxides and active metals. In this case, hydrogen of the carboxyl group is replaced by metal and salts are formed:

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$RCOOH + Mg \longrightarrow (RCOO)_2Mg + H_2$$

Carboxylates are readily hydrolyzed, like, in general, the salts of weak acids. Therefore, aqueous solutions of alkali metal salts have an alkaline reaction:

$$[CH_3COO]^-Na^+ + HOH \rightleftarrows CH_3COOH + Na^+ + HO^-$$

Mineral acids, being the strongest ones, force out carboxylic acids from their salts:

$$[CH_3COO]^-Na^+ + H^+ + Cl^- \longrightarrow CH_3COOH + Na^+ + Cl^-$$

Carboxylic acids are stable towards the action of concentrated mineral acids. An exception is formic acid, which decomposes, evolving carbon monoxide, when concentrated sulphuric acid acts on it:

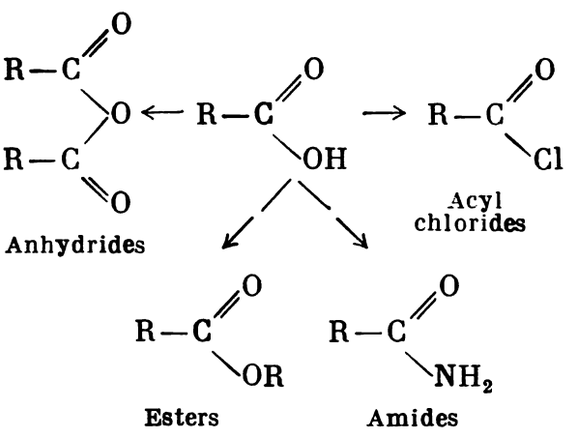
$$H-COOH \xrightarrow{H_2SO_4} CO + H_2O$$

Many properties of carboxylates have already been considered when other classes of organic compounds were being expounded: the formation of hydrocarbons in the course of fusion with alkalies, and dry distillation, which produces ketones and aldehydes.

Acids are stable with respect to heating, but if a strong electron-accepting group is attached to α-carbon, decarboxylation occurs already on heating to 100-150°C. For example, chloroform is formed, and CO_2 is eliminated, from trichloroacetic acid:

$$CCl_3-COOH \longrightarrow CHCl_3 + CO_2$$

2. Formation of functional derivatives. Functional derivatives of acids can be obtained by substituting different groups for the hydroxyl group:



A characteristic feature of these compounds is that acids are formed from them again in hydrolysis. The reactions for obtaining these derivatives, and also their properties, are considered separately.

3. Action of halogen on acids (the *Hell-Volhard-Zelinsky reaction*). α-Brominated acids are formed in the presence of bromine and small

amounts of red phosphorus:

$$\underset{\text{Propionic acid}}{CH_3-CH_2-COOH} \xrightarrow{Br_2(P)} \underset{\alpha\text{-Bromopropionic acid}}{CH_3-CHBr-COOH} + HBr$$

4. Action of reducing agents. Acids are reduced with difficulty. They are reduced to primary alcohols under the action of lithium aluminium hydride $LiAlH_4$ or diborane B_2H_6:

$$RCOOH \xrightarrow{4H} RCH_2OH + H_2O$$

Hydrogen iodide reduces them to hydrocarbons:

$$CH_3-COOH + 6HI \longrightarrow CH_3-CH_3 + 2H_2O + 3I_2$$

Acid derivatives, i.e., acyl chlorides and esters, are reduced more readily.

5. Action of oxidizing agents. Saturated acids having a normal carbon chain are oxidized with difficulty. For instance, acetic acid is used even as a solvent in oxidation reactions by the chromic-acid mixture. Formic acid, unlike other acids, is readily oxidized, and then water and CO_2 are formed:

$$H-C\begin{matrix}=O\\ -OH\end{matrix} \xrightarrow{[O]} \left[\begin{matrix}HO\\ \\ HO\end{matrix}\!\!>C=O\right] \longrightarrow H_2O + CO_2$$

In oxidation, acids with a tertiary carbon atom give hydroxy acids with the same number of carbon atoms in the molecule:

$$(CH_3)_2CH-COOH \xrightarrow{[O]} \underset{\alpha\text{-Hydroxyisobutyric acid}}{(CH_3)_2C(OH)-COOH}$$

β-Hydroxy acids are obtained under the action of hydrogen peroxide:

$$CH_3-CH_2-CH_2-COOH \xrightarrow{H_2O_2} \underset{\beta\text{-Hydroxybutyric acid}}{CH_3-CH(OH)-CH_2-COOH}$$

In animal organisms, fatty acids are also oxidized to β-hydroxy acids.

The specific properties of unsaturated acids are considered in Secs. 12.7-12.9.

12.5. Important Individual Acids. *Formic acid*, HCOOH. It was isolated in the seventeenth century from red ants living in the forest. It is contained also in the sap of stinging nettle. Anhydrous formic acid is a colourless liquid having an acrid odour and a burning taste, and it causes skin burns. It is obtained industrially by heating carbon monoxide with powdery sodium hydroxide and subsequently

treating the sodium formate formed with dilute sulphuric acid:

$$NaOH + CO \xrightarrow{200°C;\ 7\ kg/cm^2} HCOONa \xrightarrow[-NaHSO_4]{H_2SO_4} HCOOH$$

After distillation, the commercial product is 85-percent formic acid (azeotropic mixture, b.p. 107°C). To obtain formic acid of a higher concentration, a suspension of sodium formate with an excess of formic acid obtained earlier is treated with concentrated sulphuric acid. In the laboratory, anhydrous formic acid is prepared by dehydrating 85-percent acid by phosphoric anhydride.

As we have already seen, formic acid has several distinguishing features. It decomposes under the action of dehydrating substances (concentrated H_2SO_4). This reaction is used for obtaining pure carbon monoxide.

Formic acid decomposes, liberating carbon dioxide, in the presence of some finely divided metals, which are mainly of the platinum group:

$$HCOOH \longrightarrow CO_2 + H_2$$

The presence of the aldehyde group in the molecule determines the reducing properties of formic acid. It reduces the salts of some heavy metals, e.g., $HgCl_2$ to Hg_2Cl_2, and the salts of silver and palladium to free metals (it produces the silver mirror reaction). Nickel formate is reduced to free nickel:

$$(HCOO)_2Ni \xrightarrow{190°C} Ni + 2CO_2 + H_2$$

Nickel formed as fine powder is used for catalytic hydrogenation.

Formic acid is used in textile dyeing, in leather tanning, and also for various syntheses.

Sodium oxalate is formed when sodium formate is rapidly heated to 400°C:

$$\begin{matrix} HCOONa \\ + \\ HCOONa \end{matrix} \xrightarrow{400°C} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

This reaction is used for industrially obtaining oxalic acid.

Acetic acid, CH_3COOH, is widely distributed naturally; it is contained in animal secretions (urine, bile and excrements), plants (in green leaves) and sour milk and cheese, and is formed in fermentation, decay, and in the souring of wine and beer. It is formed also in the oxidation of many organic substances. Anhydrous acetic acid has a melting point of +16.6°C, and its crystals are ice-clear, and hence its name *glacial* acetic acid. It was first obtained in such form at the end of the eighteenth century by the Russian scientist T.E. Lovits. The concentration of ordinary commercial acetic acid is 70-80 per cent.

Acetic acid can be obtained by any general method of obtaining acids. It is produced industrially by oxidizing acetaldehyde by atmospheric oxygen in the presence of manganese catalysts and by subjecting liquids which contain ethyl alcohol to acetic fermentation. The last-mentioned method relates to biochemical (microbiological) processes. Under the action of *Acetobacter aceti*, whose nuclei are always present in the air, the liquids which contain alcohol "turn sour", forming natural vinegar. The process is complicated, but the reaction equation can be summed up as:

$$CH_3CH_2OH + \frac{1}{2} O_2 \longrightarrow CH_3COOH + H_2$$

Natural vinegar contains about 5 per cent of acetic acid. It is subjected to fractional distillation to obtain vinegar essence (70-80 per cent acid), which is used in the food industry for preserving vegetables, mushrooms and fish.

Acetic acid is formed also in the dry distillation of wood; this method is now important only in utilizing the wastes of the woodworking industry.

The methods of industrially obtaining acetic acid from petroleum hydrocarbons are now of great importance. In one such method, acid is obtained by directly oxidizing butane (200°C, 50 kg/cm^2):

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{O_2} 2CH_3-COOH$$

Like in many other modern processes, success wholly depends on the purity of raw material, butane in this case.

Acetic acid is obtained also from methyl alcohol by oxo synthesis in the presence of nickel tetracarbonyl $Ni(CO)_4$:

$$CH_3OH + CO \xrightarrow{Ni(CO)_4;\ \text{pressure}} CH_3COOH$$

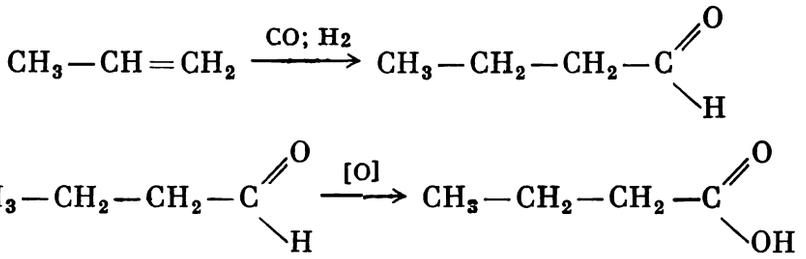
A method in which nitroethane is the starting substance has been worked out (see Sec. 14.4).

Acetic acid is characterized by stability with respect to oxidizing agents and concentrated mineral acids. It mixes in all proportions with water, alcohol, ether and benzene. Glacial acetic acid is a good solvent for many organic substances.

Acetic acid is widely employed in the chemical industry for various syntheses. Large amounts of this acid are used for obtaining esters (ethyl acetate, propyl acetate, cellulose acetate), acetic anhydride and monochloroacetic acid. Acetates of various metals have a wide application. Acetates of aluminium, chromium and iron are used as mordants for dyeing textiles. Copper salts are employed against garden, field and forest pests (Paris green). Lead salts, i.e., lead sugar $(CH_3COO)_2Pb \cdot 3H_2O$ and aqueous solution of basic lead

carbonate $(CH_3COO)_2Pb \cdot Pb(OH)_2$, are used for preparing white lead and Goulard's extract, which is employed in medicine.

Butyric acid, $CH_3CH_2CH_2COOH$. It is obtained industrially by oxidizing butyraldehyde by atmospheric oxygen in the presence of manganese catalysts. Aldehyde is prepared by oxo synthesis, i.e., from propylene and water gas. The general scheme of the reaction is:



This acid is obtained also in saccharide fermentation (butyric fermentation).

Butyric acid is contained in cow butter (2.4 per cent) as glycerol ester, from which it was first isolated (Chevreul, 1814). When butter turns rancid (as a result of it being kept for a long time), free butyric acid, which imparts a repugnant odour and taste to butter, is formed together with other decomposition products. Free butyric acid is contained in perspiration (the repugnant odour of perspiration is that of butyric acid).

Besides butyric acid, the composition of natural fats and oils includes as glycerol esters also other fatty acids with a normal chain and an even number of carbon atoms in the molecule (C_6-C_{24}). For example, *caproic acid* $CH_3(CH_2)_4COOH$ is contained in goat butter. Hence the name of the acid (the Latin word "caper" means "goat"). The composition of fats and their properties are considered at greater length in Sec. 12.22.

Acids having an odd number of carbon atoms and iso structures are seen more rarely in nature, being found mainly in essential oils, e.g., *isovaleric acid* is found in the essential oil of the valerian roots.

The derivatives of caproic and *enanthic*, $CH_3(CH_2)_5COOH$, acids are used for obtaining synthetic polyamide fibres.

Palmitic and *stearic* acids, being high-molecular-weight acids, are especially important among fatty acids:

$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$
Palmitic acid	Stearic acid

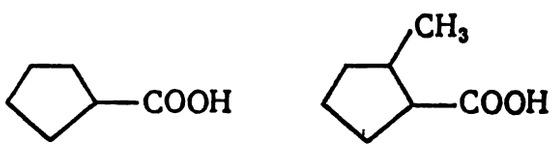
The glycerides of these acids are the main constituent of natural fats and oils.

Large amounts of higher fatty acids are now being obtained by paraffin oxidation, which is effected by blowing air through molten paraffin in the presence of manganese oxides at 100°C. After washing, lower acids (C_1-C_4) pass into solution, from where they are separated

by distillation. Higher fatty acids (C_5-C_{22}) are neutralized, and then they are isolated under the action of sulphuric acid and distilled off. About 50-60 kg of lower and 600-700 kg of higher acids are obtained from 1000 kg of paraffin.

Fatty acids obtained from petroleum are employed in technological processes. They are used to produce soaps and lubricants for metal protection, and are employed in the mining and metal-processing industries and for making rubber, linoleum, and paint and varnish articles.

Naphthenic acids are obtained from petroleum (discovered by V. V. Markovnikov in 1892). Natural oil contains a small amount (up to 1 per cent) of these acids. They are mainly alicyclic acids having a five-membered ring: cyclopentane carboxylic acid and its homologues, e.g.,



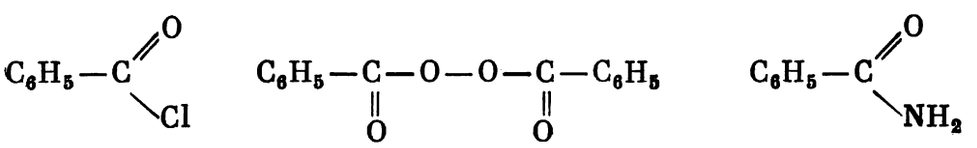
Sodium salts of these acids are formed when petroleum products are being refined by alkali; these salts possess detergency and are called *naphthene soap*.

Naphthenates of cobalt, manganese, lead and other metals, known as *siccatives*, are used as catalysts for hardening drying oils (see Sec. 12.22).

Benzoic acid, C_6H_5—COOH, is the most important representative of aromatic acids. It is widely distributed naturally in the vegetable kingdom: in balsams, ladanums and essential oils. It is contained in animal organisms in protein decay products. It is a crystalline substance having a melting point of 122°C, and readily sublimes. It is sparingly soluble in cold water, but its water-solubility increases as temperature rises; it dissolves well in alcohol and ether

It is obtained industrially by oxidizing toluene or other benzene homologues having a single side chain in the molecule, and by hydrolyzing benzotrichloride C_6H_5—CCl_3.

Benzoic acid, like fatty acids, forms functional derivatives which are usual for acids, i.e., benzoyl chloride I, benzoyl peroxide II, and benzamide III:



I II III

In addition, benzoic acid can undergo substitution reactions in the ring, i.e., halogenation, nitration and sulphonation. The carboxyl group is a *meta*-directing substituent, and therefore *meta*-derivatives, such as *m*-bromobenzoic acid and *m*-nitrobenzoic acid, are formed in electrophilic substitution reactions.

12.6. Soaps and Detergents. The salts of higher fatty acids are known as *soaps*. Ordinary solid soap is a mixture of sodium salts of mainly palmitic and stearic acids. Liquid *green soap* is formed when potassium salts are mixed together. Soaps are obtained from vegetable and animal fats by hydrolyzing (saponifying) them in an alkaline medium, or from synthetic fatty acids:

$$\text{Fat} \xrightarrow[\text{alkaline medium}]{\text{hydrolysis in an}} \text{Glycerol} + \text{Salts of fatty acids (soap)}$$

Solid fats (natural fats and those obtained by hydrogenating liquid fats) yield solid soaps. Liquid oils (which contain many unsaturated liquid acids) give softer soaps.

The detergency of soap is connected with its *surface activity*, i.e., with its ability to sharply reduce the surface tension of water, causing the surfaces (or particles) to be wetted and promoting the formation of emulsions, suspensions, etc. This is a complicated physicochemical process.

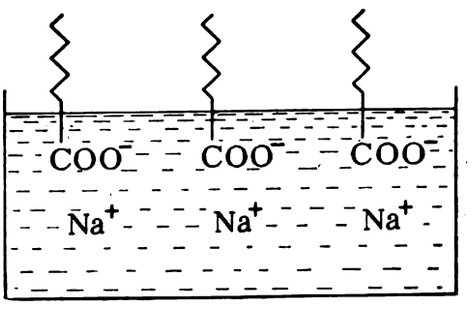


Fig. 12.3. Distribution of molecules in soap solutions

Any soiling is *hydrophobic* (water-repellent); water does not wet it, but slides off it in the form of drops. The wettability of water increases if a soap solution or some other surfactant substance is added to it.

Soap molecules, R—COONa, are made out of a *hydrophobic* group, i.e., a hydrocarbon radical R which has little affinity for water, and a polar, or *hydrophilic* (having affinity for water), group COONa. The hydrophilic group is immersed in water, while the hydrophobic one is pushed out from it (Fig. 12.3). Owing to such an orientation of soap molecules at the interface, surface tension decreases, while the wettability, frothiness and, consequently, detergency of a soap solution increase.

Ordinary soaps have different detergency in hard and soft water. In hard water (which is rich in the salts of calcium, magnesium and iron), flakes of insoluble salts are formed and the detergency of soap diminishes:

$$2C_{17}H_{35}COONa + Ca^{2+} \longrightarrow (C_{17}H_{35}COO)_2Ca + 2Na^+$$

In sea water, washing cannot be done with ordinary soap. The precipitate of calcium and magnesium salts makes the textile rigid.

Another disadvantage of soap is that it is partially hydrolyzed as a salt of a weak acid when water acts on it, causing the formation of an alkaline medium, which is detrimental to some types of textile.

Synthetic detergents are now used for household washing and for washing wool and textiles in industry; these detergents possess greater detergency than soap, and they do not spoil textiles and can be used in hard and sea water.

The molecules of synthetic detergents, like soap, contain a polar hydrophilic group (but of a different nature) which is bound with the hydrocarbon radical. Like in ordinary soap, the hydrocarbon radical is in the C_{12}-C_{18} range.

It is not food fats, but petroleum refining products, which are raw material for obtaining synthetic detergents. Besides higher fatty acids, higher fatty alcohols are formed as by-products when paraffin is oxidized by air. Higher fatty alcohols can be obtained also by catalytically hydrogenating higher fatty acids:

$$RCOOH \xrightarrow{+H_2} RCH_2OH$$

Higher fatty acids form acid esters called alkylsulphuric acids under the action of concentrated sulphuric acid. These acids possess strong acidic properties and, with alkalies, yield salts known as *alkyl sulphates*:

$$RCH_2OH \xrightarrow{+H_2SO_4} RCH_2-OSO_3H \xrightarrow{NaOH} RCH_2-OSO_3Na$$

These salts possess excellent detergency.

Sulphochlorides are formed when paraffins are subjected to photochemical sulphochlorination (see Sec. 2.6); sulphonates known as *alkyl sulphonates* RSO_3Na, which are also good detergents, are obtained from them under the action of alkali.

Alkyl aryl sulphonates are obtained from aromatic hydrocarbons having a long side chain by subjecting them to sulphonation and subsequent alkali treatment:

$$C_8H_{17}-C_6H_5 \xrightarrow{H_2SO_4} C_8H_{17}C_6H_4SO_2OH \xrightarrow{NaOH} C_8H_{17}C_6H_4SO_2ONa$$

Alkyl sulphates, alkyl sulphonates and alkyl aryl sulphonates can be used in hard water (their calcium salts are soluble). They are not hydrolyzed, being salts of strong acids, and thus an alkaline medium is not created. The composition of such surfactants can include not only sodium, but also potassium, ammonium, organic bases, e.g., amines, and others as a cation.

The foregoing types of compounds constitute the group of anionic-active detergents. There are also other detergents: cationic-active, amphoteric, etc.

Modern synthetic detergents are complex compositions which include surfactants, phosphates, silicates, soda, aromatic substances, and optical bleaching agents for making a textile more white.

The detergency of synthetic detergents is approximately ten times higher than that of ordinary soap. In recent years, the production of synthetic detergents has sharply grown, while that of ordinary soap has dropped.

UNSATURATED MONOBASIC ACIDS

12.7. Isomerism. Preparation Methods. There are multiple bonds in the molecules of unsaturated acids, i.e., in the radical linked with the carboxyl group. Unsaturated acids with a single double bond in the molecule have the general formula of $C_nH_{2n-1}COOH$. The simplest of them is *acrylic acid* $CH_2=CH-COOH$. The isomerism of its homologues is engendered by the isomerism of the carbon skeleton and the position of the double bond relative to the carboxyl. For example, acids of the C_3H_5COOH composition are known to have the following isomers:

$CH_3-CH=CH-COOH$	$CH_2=C(CH_3)-COOH$	$CH_2=CH-CH_2-COOH$
Crotonic acid (2-butenoic acid)	Methacrylic acid (2-methyl-2-propenoic acid)	Vinylacetic acid (3-butenoic acid)

In addition, like other ethylene compounds, unsaturated acids can undergo *cis-trans*-isomerism:

$CH_3-C(H)=C(H)-COOH$	$CH_3-C(H)=C(COOH)-H$
trans-Isomer crotonic acid (m.p. 72°C; b.p. 189°C)	*cis*-Isomer isocrotonic acid (m.p. 15.5°C; b.p. 172°C)

Unsaturated acids can be obtained by the following methods:

1. From substituted saturated acids by the formation of a double bond in the radical:

(a) By dehydrohalogenating halogen-substituted acids:

$$\left.\begin{array}{l} CH_3-CH_2-CHCl-COOH \\ \text{α-Chlorobutyric acid} \\ CH_3-CHCl-CH_2-COOH \\ \text{β-Chlorobutyric acid} \end{array}\right\} \xrightarrow[-HCl]{KOH;\ alcohol} CH_3-CH=CH-COOH \quad \text{Crotonic acid}$$

(b) By dehydrating hydroxy acids:

$$HOCH_2-CH_2-COOH \xrightarrow[-H_2O]{} CH_2=CH-COOH$$

β-Hydroxypropionic acid — Acrylic acid

Reactions for compounds containing groups being eliminated in the β-position (Cl, OH, etc.) occur especially readily.

2. From halogen-containing unsaturated compounds by synthesis via nitriles:

$$CH_2=CH-CH_2Cl \xrightarrow{KCN} CH_2=CH-CH_2-CN \xrightarrow{H_2O(H^+)} CH_2=CH-CH_2-COOH$$

12.8. Physical and Chemical Properties. Unsaturated acids are more acidic than the corresponding saturated ones. For example, acrylic acid is approximately four times stronger than propionic acid.

The effect of the multiple bond is especially strong if it is in the α,β-positions relative to the carboxyl. In this case, the proton is eliminated more readily, because the stable carboxylate anion $\overset{\beta}{C}H_2=\overset{\alpha}{C}H-C(=O)-O^-$ is formed. The effect of the multiple bond diminishes as it moves away from the carboxyl group.

Several properties of unsaturated acids are engendered by the properties of the carboxyl group (the *formation of salts*, *esters*, etc.) and the double bond (*addition reactions*). Specific properties are possessed by acids having a double bond which is close to the carboxyl, i.e., by α,β-unsaturated acids. For example, they undergo hydrogen halide addition and hydration, contrary to Markovnikov's rule, according to the type of 1,4-addition (like in conjugated systems):

$$\overset{\beta}{C}H_2=\overset{\alpha}{C}H-COOH \xrightarrow{HBr} CH_2Br-CH_2-COOH$$

β-Bromopropionic acid

$$\overset{\beta}{C}H_2=\overset{\alpha}{C}H-COOH \xrightarrow{H_2O(H^+)} CH_2OH-CH_2-COOH$$

β-Hydroxypropionic acid

At the first step, the proton is added to oxygen of the carboxyl group, and the nucleophile attacks β-carbon, while the double bond passes over to the positions 2,3. The intermediate product is then isomerized:

$$\overset{\delta+}{C}H_2=\overset{\delta-}{C}H-\overset{\delta+}{C}(OH)=\overset{\delta-}{O} + H^+ + Br^- \longrightarrow \left[CH_2Br-CH=C(OH)(OH)\right] \longrightarrow CH_2Br-CH_2-COOH$$

The addition reaction of bromine (or iodine) is characteristic of unsaturated acids. The number of multiple bonds can be determined by the amount of bromine or iodine that is added. Other addition reactions occur similarly.

Unsaturated acids, unlike sparingly oxidizable saturated acids and like olefins, are readily oxidized. When they are carefully oxidized by an alkaline solution of potassium permanganate, dihydroxy acids are formed:

$$\underset{\text{Acrylic acid}}{CH_2=CH-COOH} \xrightarrow{[O];\ H_2O} \underset{\text{Dihydroxypropionic acid}}{CH_2OH-CHOH-COOH}$$

When oxidation occurs vigorously, the molecule is cleaved at the site of the double bond and a mixture of various products, by which the site of the double bond can be determined, is formed. The position of the double bond in oleic acid was determined in this way:

$$\underset{\text{Oleic acid}}{CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH} \xrightarrow{[O]} \longrightarrow \underset{\text{Pelargonic acid}}{CH_3-(CH_2)_7-COOH} + \underset{\text{Azelaic acid}}{HOOC-(CH_2)_7-COOH}$$

12.9. Important Individual Acids. *Acrylic (propenoic)* acid is a liquid having a pungent odour; its b.p. is 140°C, m.p., +13°C, and d_4^{20}, 1.06. It mixes with water in all proportions. It is produced industrially by hydrolyzing acrylonitrile

$$CH_2=CH-CN \xrightarrow{H_2O} CH_2=CH-COOH$$

or is obtained from acetylene by the carbonylation reaction (*Reppe reaction*)

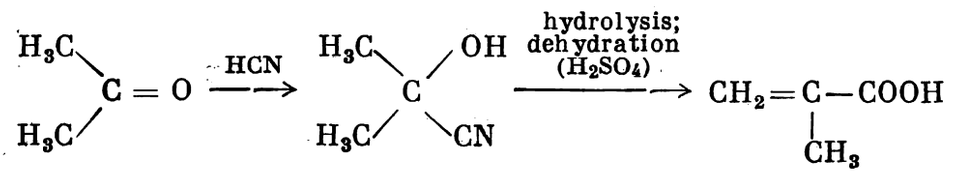
$$CH\equiv CH+CO+H_2O \xrightarrow{Ni(CO)_4;\ Cu_2Cl_2} CH_2=CH-COOH$$

The acid itself and its derivatives (acrylonitrile, esters) are readily polymerized and serve as raw material for obtaining various high-molecular-weight compounds.

In industry, wide use is made of the methyl ester of acrylic acid, *methyl acrylate*, which is readily polymerized with the formation of transparent products. It is obtained from acrylonitrile and methyl alcohol in the presence of sulphuric acid:

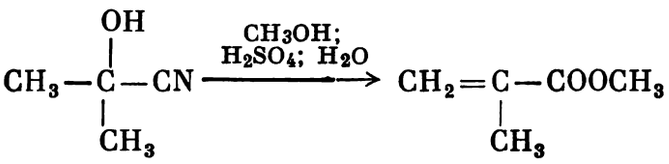
$$CH_2=CH-CN \xrightarrow[H_2SO_4;\ H_2O]{CH_3OH;} CH_2=CH-COOCH_3$$

Methacrylic acid is a liquid whose b.p. is 160°C, m.p., 15°C, and d_4^{20}, 1.05. It is obtained industrially from acetone and hydrocyanic acid:



The derivatives of methacrylic acid also serve as monomers in polymerization reactions.

The most important derivative is *methyl methacrylate*, which is obtained by heating acetone cyanohydrin with methyl alcohol in the presence of H_2SO_4:



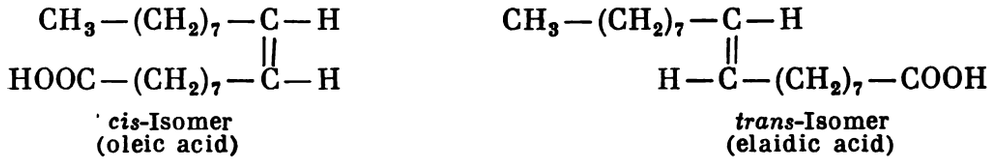
Polymethyl methacrylate, or Plexiglas, is obtained when methyl methacrylate is polymerized (see Sec. 23.4).

Sorbic acid is a representative of acids having two double bonds in the molecule, its formula being $CH_3—CH=CH—CH=CH—$ —COOH. It is a crystalline substance with a melting point of 134°C. It is found naturally and produced synthetically (see Sec. 12.12). Sorbic acid is a valuable preservative for foodstuffs. In a concentration of about 0.1 per cent, it preserves meat and fish products, finished culinary products and cheese, precludes the souring of fruit and berry juices, syrups, wines, etc.

Oleic acid, $C_{17}H_{33}COOH$, is one of the most important higher unsaturated acids. It is very widely distributed naturally: it is in the composition of all fats as esters with glycerol (in some fats, it constitutes up to 50 per cent of the total mass of acids). It is a colourless liquid which solidifies in the cold (m.p. 14°C). Two geometric isomers, *cis-* and *trans-* correspond to its general formula:

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$$

Oleic acid is a *cis*-isomer. The *trans*-isomer is known as elaidic acid.



Elaidic acid is not found naturally. It can be obtained from oleic acid under the catalytic action of nitrous acid. Unlike oleic acid, it is a solid and has a melting point of 51-52°C.

Linoleic acid, $C_{17}H_{31}COOH$, and *linolenic acid*, $C_{17}H_{29}COOH$, are in the composition of vegetable oils. For example, linseed oil contains about 25 per cent of linoleic acid and up to 58 per cent of linolenic acid. Both acids yield stearic acid when they are hydrogenated, and this confirms the normal structure of their carbon skele-

ton:

$$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$$

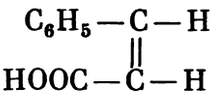
Linoleic acid (m.p. −5°C)

$$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$$

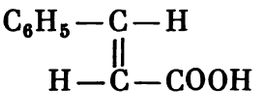
Linolenic acid (m.p. 11°C)

Both acids are readily oxidized by atmospheric oxygen and are polymerized (see Sec. 12.22).

Cinnamic acid, $C_6H_5-CH=CH-COOH$, is known as two isomers which have different physical constants:

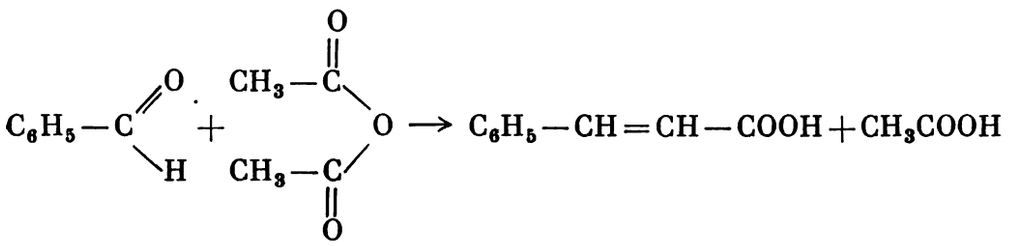


cis-Cinnamic (m.p. 57°C)



trans-Cinnamic (m.p. 133°C)

An important method of obtaining cinnamic acid is by condensing benzaldehyde with acetic anhydride in the presence of sodium acetate (*Perkin's reaction*):



Cinnamic acid is in the composition of the aromatic balsam resin called *styrax* (ladanum). When cinnamic acid is heated, it decarboxylates and an important commercial product called *styrene* is formed (Sec. 7.7):

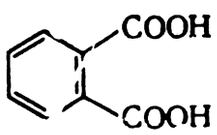
$$C_6H_5-CH=CH-COOH \longrightarrow C_6H_5-CH=CH_2+CO_2$$

DIBASIC ACIDS

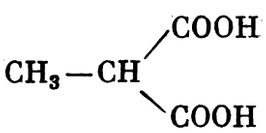
The simplest representative of this series of acids is *oxalic acid*, HOOC—COOH; its closest homologue is *malonic acid*, HOOC—CH_2—COOH, in which the carboxyl groups are separated by the CH_2 group. By elongating the chain successively by one CH_2 group, we can obtain a series of dibasic acids.

12.10. Nomenclature. General Methods of Preparation. Physical Properties. Many acids have trivial names (Table 12.3). In modern international nomenclature, the names of dibasic acids have the suffix **dioic** or **dicarboxylic** followed by the word "acid". For example, oxalic acid is called ethanedioic acid; malonic acid, propanedioic or methanedicarboxylic acid, etc. However, trivial names are most commonly used.

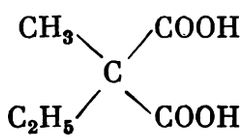
TABLE 12.3. **Physical Properties of Some Dicarboxylic Acids**

Name of acid	Formula	Melting point, °C	Solubility at 20°C, g/100g H_2O	Constants of dissociation in water at 25°C	
				$K_{a_1} \cdot 10^{-5}$	$K_{a_2} \cdot 10^{-5}$
Oxalic	HOOC—COOH	189.5	8.6	5900	6.4
Malonic	HOOC—CH_2—COOH	135.6	73.5	149	0.22
Succinic	HOOC—$(CH_2)_2$—COOH	185.0	5.8	6.6	0.25
Glutaric	HOOC—$(CH_2)_3$—COOH	97.5	63.9	4.7	0.29
Adipic	HOOC—$(CH_2)_4$—COOH	152	1.5	3.7	0.24
Pimelic	HOOC—$(CH_2)_5$—COOH	105	5.0	3.3	—
Maleic (*cis*-)	HOOC—CH=CH—COOH	130	79	1420	—
Fumaric (*trans*-)	Ditto	288	0.7	93	—
Phthalic		206-208 (decom.)	—	112	—

A homologous series having a mutual arrangement of carboxyl groups that is the same for all the members of the series can be derived from each member of a series of dibasic acids (except oxalic acid):



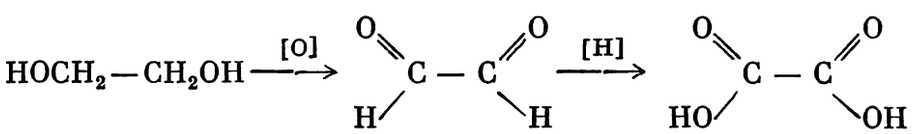
Methyl malonic acid



Methyl ethyl malonic acid

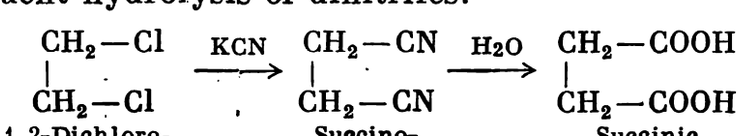
Two of the general methods of obtaining dibasic acids are given below:

1. Oxidation of diprimary glycols. The reaction occurs via the intermediate formation of dialdehyde:



Ethylene glycol — Glyoxal — Oxalic acid

2. The action of potassium cyanide on dihalogen derivatives with the subsequent hydrolysis of dinitriles:



1,2-Dichloroethane — Succinodinitrile — Succinic acid

Dibasic acids are crystalline substances. The lower members of the series are considerably well soluble in water. Solubility decreases as the number of carbon atoms in the molecule increases, but compounds with an odd number of carbon atoms have higher solubility. The melting points of compounds with an even number of carbon atoms are higher than those of their neighbours with an odd number of carbon atoms (see Sec. 12.3).

In an aqueous solution, dicarboxylic acids are dissociated successively:

$$HOOC-COOH \rightleftarrows (HOOC-COO)^- + H^+$$

$$(HOOC-COO)^- \rightleftarrows (OOC-COO)^{2-} + H^+$$

Table 12.3 gives both dissociation constants. Dibasic acids are stronger than monobasic ones. The effect of one carboxyl on the acidity of another is the greater, the closer they are to one another in the molecule. The strongest is oxalic acid (which is stronger than acetic acid by about 2000 times). The second dissociation constant of acids is considerably lower than the first one (the second proton is torn away with greater difficulty).

12.11. Chemical Properties. Dicarboxylic acids are similar to monocarboxylic ones by their general chemical properties: they form salts, esters, acyl chlorides, etc. Acid and neutral salts, acid and neutral esters, and so forth, are obtained, depending on whether one or two carboxyls enter into a reaction.

The mutual arrangement of carboxyl groups in the molecule affects the properties of compounds, engendering their specific behaviour. The possibility of interaction between carboxyl groups is greater when they are close together. Their mutual effect is weak when they are separated by a chain of six or more carbon atoms.

Among their specific properties their behaviour towards heating should be noted, the nature of transformations depends on the distance between the carboxyl groups.

Oxalic acid, where the carboxyl groups are in the positions 1,2, is decarboxylated when rapidly heated, forming formic acid and carbon dioxide. If oxalic acid is heated in the presence of concentrated sulphuric acid, formic acid also decomposes:

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow{200^\circ C} \begin{cases} \longrightarrow CO_2 + HCOOH \\ \xrightarrow{H_2SO_4} CO_2 + CO + H_2O \end{cases}$$

Malonic acid and its homologues, i.e., acids in whose molecules the carboxyl groups are in the positions 1,3 (both carboxyl groups are linked with a single carbon atom), are readily decarboxylated

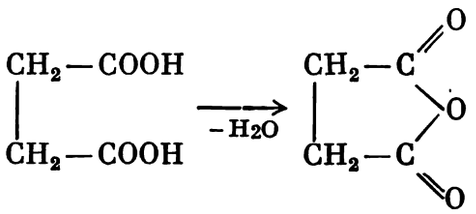
with the formation of monobasic acetic acid and its homologues:

$$HOOC-CH_2-COOH \xrightarrow[-CO_2]{} CH_3-COOH$$

$$HOOC-\underset{\displaystyle R}{\underset{|}{CH}}-COOH \xrightarrow[-CO_2]{} R-CH_2-COOH$$

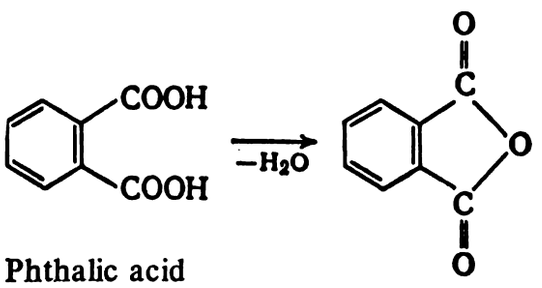
The closeness of the carboxyl groups makes compounds thermally unstable.

Water is eliminated and internal cyclic anhydrides having five- and six-membered rings are formed when *succinic* and *glutaric* acids or their homologues, i.e., compounds in which the carboxyl groups are in the positions 1,4 and 1,5, are heated:



Succinic acid — Succinic anhydride

Aromatic *o*-dicarboxylic acid, or *phthalic acid*, also acts in the same way:



Phthalic acid — Phthalic anhydride

12.12. Important Individual Diacids. *Oxalic acid* exists usually as a crystal hydrate, $HOOC-COOH \cdot 2H_2O$, whose melting point is 101°C; anhydrous acid melts at 189.5°C. It is found naturally as oxalates and in a free state. Calcium oxalate is contained in all plants, while potassium acid salt, KOOC—COOH, in dock, in oxalis. Oxalates of alkaline metals dissolve in water, while calcium oxalate practically does not dissolve in cold water. When metabolism is upset in the human organism, calcium oxalate accumulates, causing the formation of stones in the liver, kidneys and urinary tracts.

The low solubility of calcium oxalate is used in analytical chemistry for qualitatively and quantitatively determining calcium.

Characteristic properties of oxalic acid are the above-mentioned ability to become decarboxylated on heating and its ready oxidizability. Being a product of oxidation of many organic substances, oxalic acid itself is readily oxidized, for example, by potassium permanganate:

$$HOOC-COOH \xrightarrow{[O]} CO_2+H_2O$$

This property is used, for example, in analytical chemistry for preparing standard solutions of potassium permanganate. Oxalic acid is used industrially for dyeing textiles and removing rust stains and inkblots from them, and also as a bleaching agent.

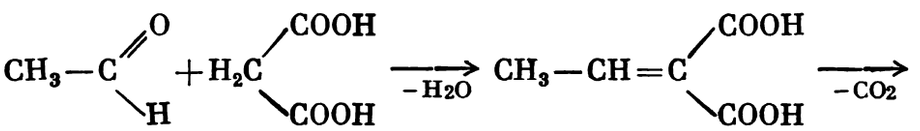
The industrial method of obtaining oxalic acid, i.e., by heating sodium formate, was considered earlier (see Sec. 12.5).

Malonic acid. It is obtained industrially from monochloroacetic acid via its mononitrile with subsequent hydrolysis:

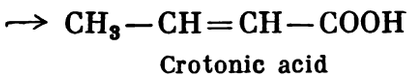
$$Cl-CH_2-COOH \xrightarrow{KCN} NC-CH_2-COOH \xrightarrow{H_2O} HOOC-CH_2-COOH$$

Carboxyl groups have an activating effect on the hydrogen atoms of the CH_2 group which is between them. The heightened reactivity of hydrogen atoms affects the properties of the acid itself and those of its esters, and this is used in various syntheses.

For example, when malonic acid is condensed with aldehydes and ketones, it gives α,β-unsaturated acids:

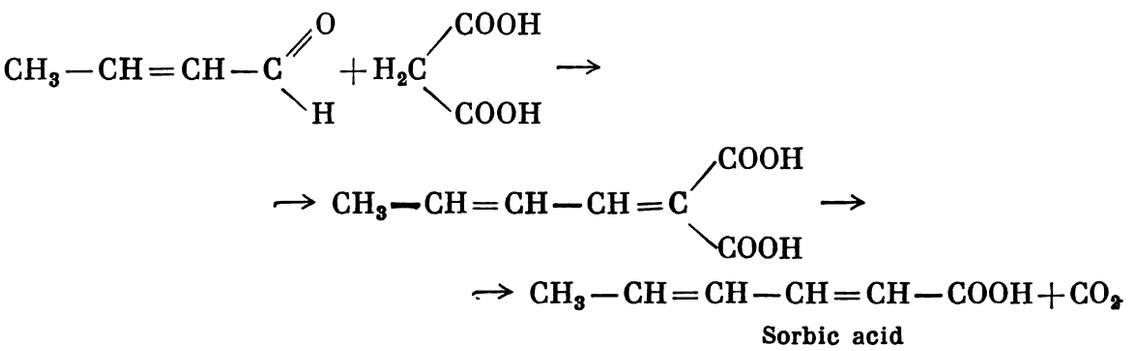


Ethylidene malonic acid



Crotonic acid

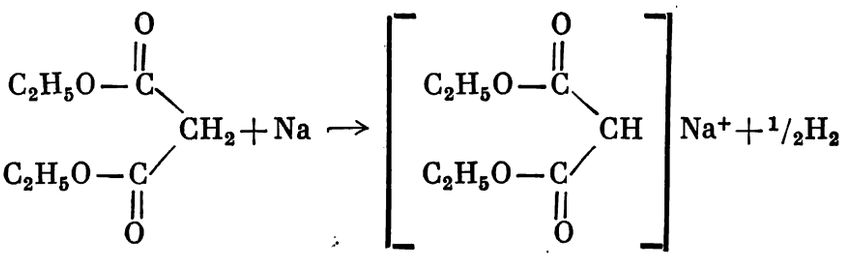
Polyene acids are obtained from unsaturated aldehydes by this reaction:



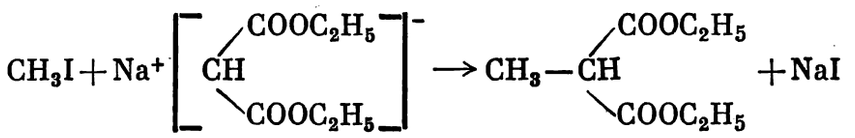
Sorbic acid

The most important derivative of malonic acid is its diethyl ester, or *malonic ester*. This liquid with a pleasant odour (b.p. 199°C) is widely used for various laboratory syntheses.

Sodiomalonic ester is obtained when metallic sodium or sodium ethoxide acts on malonic ester:

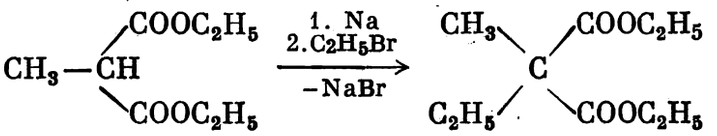


Sodiomalonic ester is readily alkylated by halogen derivatives, forming derivatives that are substituted at carbon:



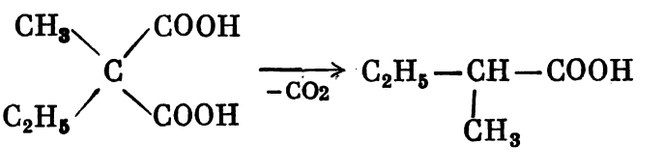
Sodiomalonic ester — Methyl malonate

In the ester obtained, the hydrogen atom of the CH group can also be replaced by sodium and then again by the hydrocarbon radical, as a result of which esters of dialkyl malonic acids are formed:



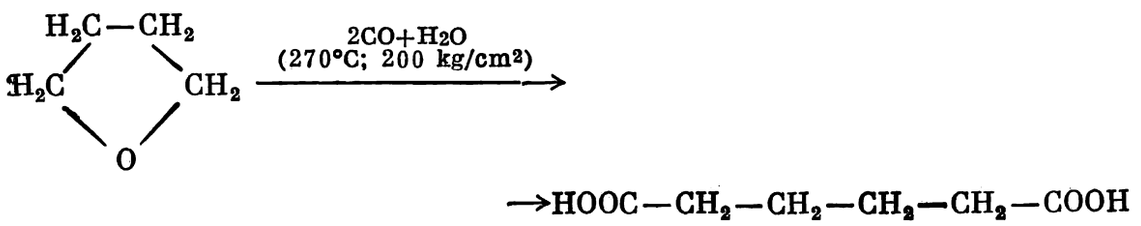
Methyl ethyl malonate

When alkyl and dialkyl malonates are hydrolyzed, the corresponding substituted malonic acids are formed (Conrad synthesis). When these acids are decarboxylated, monobasic acids, the homologues of acetic acid, are obtained:



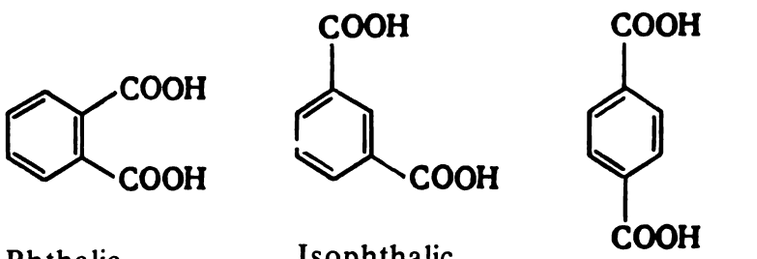
Methyl ethyl acetic acid

Adipic acid, HOOC—$(CH_2)_4$—COOH, is readily soluble in alcohol and sparingly soluble in water and ether. It is obtained industrially by oxidizing cyclohexanol, cyclohexanone or cyclohexane (see Sec. 3.4), and also from the heterocyclic compound called tetrahydrofuran in the presence of nickel tetracarbonyl [$Ni(CO)_4$]:



Large amounts of adipic acid are used for obtaining the synthetic fibre called nylon. In the food industry, adipic acid can replace citric and tartaric acids. Adipic acid esters, i.e., butyl adipinate and octyl adipinate, are used as plasticizers for producing plastics.

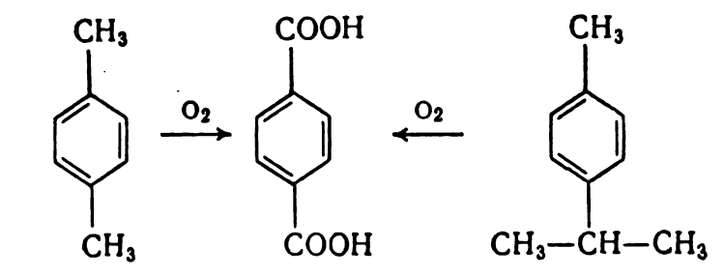
Phthalic acids. When aromatic hydrocarbons containing two side chains in the molecule are oxidized, three isomeric dicarboxylic acids, called phthalic acids, can be obtained, depending on the arrangement of the side chains:



Phthalic Isophthalic Terephthalic

Phthalic acid is a crystalline substance which melts at 206-208°C (decomposition), and it dissolves in hot water. It is obtained by oxidizing naphthalene. Phthalic anhydride is obtained practically instantaneously (see Sec. 7.10). Wide use is now made of diesters of phthalic acid, i.e., dibutyl phthalate and dioctyl phthalate, which have very low vapour pressure and high boiling points. They are used instead of mercury in vacuum and diffusion pumps and as plasticizers for producing plastics.

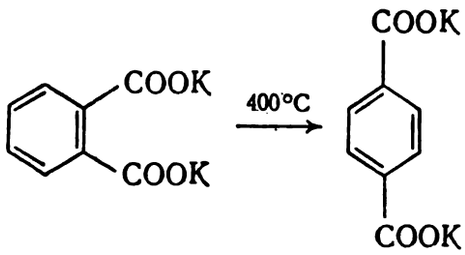
Terephthalic acid sublimes without melting when it is heated to 300°C; it is sparingly soluble in water and organic solvents. It is obtained industrially by oxidizing *p*-xylene or cymene, which is isolated from turpentine:



p-Xylene Terephthalic acid Cymene

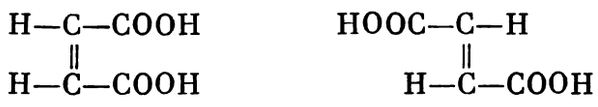
An important method of obtaining terephthalic acid is by isomerizing potassium phthalate in the presence of a catalyst (zinc and

cadmium phthalate):



Terephthalic acid is used as raw material for obtaining the synthetic Terylene fibre (see Sec. 23.8).

Maleic and fumaric acids are unsaturated dibasic acids. They are geometric isomers:



cis-Isomer Maleic acid (m.p. 130 °C) — *trans*-Isomer Fumaric acid (m.p. 288 °C)

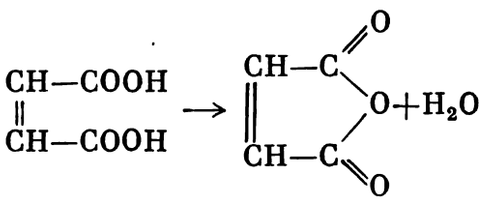
The *cis-trans*-isomerism of ethylene compounds was thoroughly studied precisely on the basis of these acids.

Maleic acid is less stable than fumaric acid. It passes into fumaric acid, which is more stable, under the action of some substances (traces of iodine, bromine and nitrous acid). Fumaric acid passes into maleic acid under the action of ultraviolet light or when it is heated, i.e., energy must be supplied for this conversion.

Fumaric acid is sparingly soluble in water (less than 1 per cent), while maleic acid is well-soluble in it (about 50 per cent). Maleic acid is stronger than fumaric acid.

Both acids produce characteristic reactions for the double bond (they decolorize bromine water and potassium permanganate), and also reactions for the carboxyl groups, as a result of which two series of derivatives (acid and neutral salts, acid and neutral esters, etc.) are obtained.

Both acids are reduced by hydrogen to succinic acid. All this proves that they have the same chemical structure. But a cyclic anhydride is formed only from maleic acid, as is confirmed by its *cis*-structure:

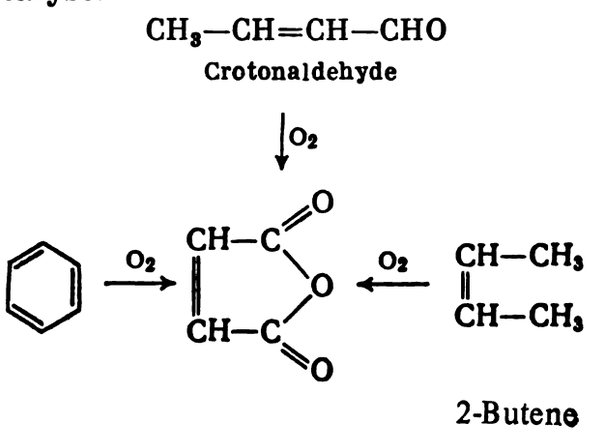


Maleic acid — Maleic anhydride

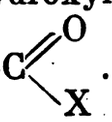
In the *trans*-arrangement, the carboxyl groups are too far away from one another to form cyclic anhydride.

Fumaric acid is widespread naturally: it is found in mushrooms, lichens and, in an inconsiderable amount, in animal cells, and it participates in metabolism. Maleic acid has not been found naturally, and it is poisonous.

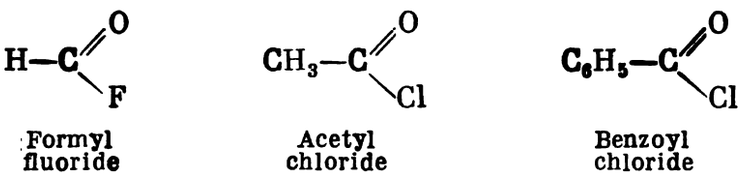
Maleic acid is obtained industrially as maleic anhydride when some substances are oxidized by atmospheric oxygen in the presence of a vanadium catalyst:



ACYL HALIDES

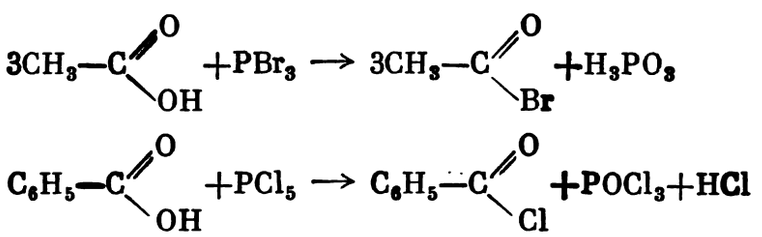
Acyl halides are the derivatives of acids in which the hydroxyl of the carboxyl group is replaced by the halogen  .

12.13. Nomenclature. Preparation Methods. Properties. The names of acyl halides are composed like those of alkyl halides, but the name of an acyl group is taken as the basis, e.g.,

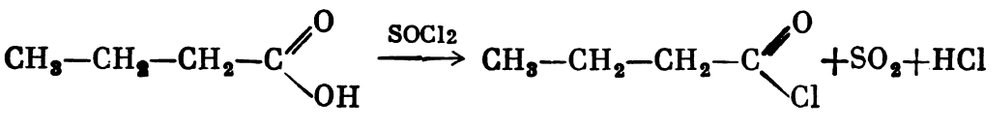


They are obtained in various ways. The selection of a reagent is connected with the method of separating the products being obtained: the boiling point of the acyl halide being obtained should differ from that of the by-products. The following methods are used in practice:

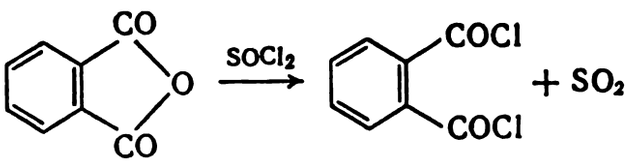
1. Action of phosphorus halides on acids:



2. The action of thionyl chloride, $SOCl_2$, on acids or acid anhydrides in the presence of pyridine as a catalyst:



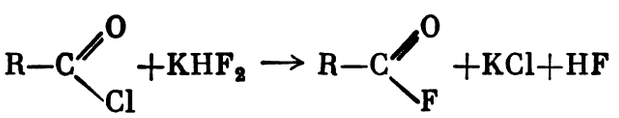
Butyric acid — Butyryl chloride



Phthalic anhydride — Phthalyl chloride

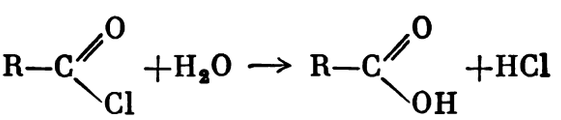
This method is convenient, because gaseous substances are formed as by-products, and therefore it is easy to obtain the reaction product in its pure form.

Acid fluorides are obtained from acid chlorides in the reaction of exchange with KHF_2:

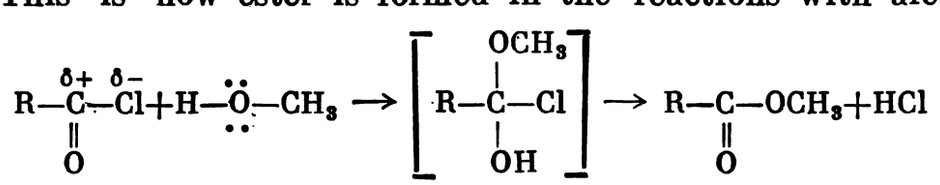


Acid iodides are poorly stable. The most important ones are acid chlorides.

Chlorides of lower acids are liquids having a pungent odour, and chlorides of higher acids are solids. They do not dissolve in water, but enter into a hydrolysis reaction with it. For example, many liquid acid chlorides fume in the air, and acid droplets are formed when they interact with atmospheric moisture:

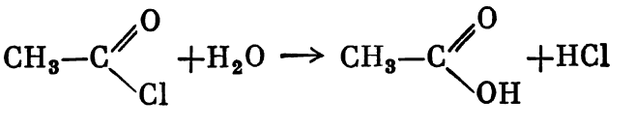


These substances are very reactive. Their reaction centre is carbonyl carbon, which bears a considerably high positive charge. This charge originates under the action of two highly electronegative atoms: oxygen and chlorine. Therefore, carbonyl carbon readily reacts with nucleophilic reagents. At the initial stage, the nucleophilic reagent (water, alcohol, amine) is added along the double bond C=O. Hydrogen chloride is then eliminated from the intermediate product. This is how ester is formed in the reactions with alcohols:



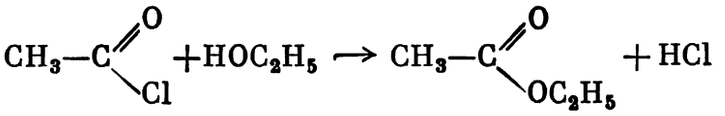
As a result of the reaction, an *acyl group* is introduced into the molecule of an organic compound. These reactions are known as *acylation* reactions. They include:

1. Acylation of water (hydrolysis), resulting in the formation of acids:



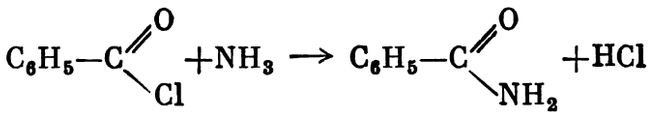
Acetyl chloride — Acetic acid

2. Acylation of alcohol (alcoholysis), resulting in the formation of esters:



Ethyl acetate

3. Acylation of ammonia (ammonolysis), resulting in the formation of acid amides:



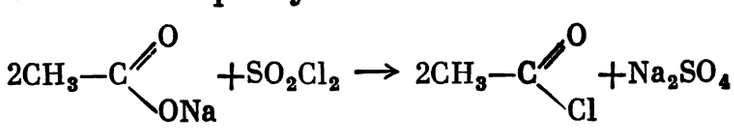
Benzoyl chloride — Benzamide

4. The acylation of aromatic hydrocarbons (ketone synthesis by the Friedel-Crafts method) has already been considered earlier (see Sec. 11.2).

12.14. Individual Acyl Halides. The simplest representative of acid chlorides is *formyl chloride*, HCOCl. This anhydride has not been isolated in its free state (it decomposes into CO and HCl), but certain reactions, such as the Gattermann reaction (see Sec. 11.2), show that it may exist in a free state.

Formyl fluoride, HCOF, is a gas which has a strong odour and liquefies at —26°C. At room temperature, it decomposes into CO and HF. It was first obtained by A. N. Nesmeyanov from benzoyl fluoride and formic acid.

Acetyl chloride, CH_3COCl, is a liquid which boils at 51°C. It fumes in the air and reacts vehemently with water. It is widely used as an acetylating agent. It is obtained industrially from anhydrous sodium acetate and sulphuryl chloride:



Benzoyl chloride, C_6H_5COCl, is a liquid which boils at 197°C and has an unpleasant irritating odour. It is obtained when PCl_5 acts on benzoic acid (Sec. 12.13) or when chlorine acts on benzal-

dehyde (Sec. 11.5). It is used as a benzoylating agent in various syntheses.

Phosgene, $COCl_2$, is an absolute chloride of carbonic acid; it boils at 8.3°C and has an odour of fresh hay; obtained industrially from carbon monoxide and chlorine in the presence of activated charcoal:

$$CO+Cl_2 \xrightarrow{200\,^{\circ}C} Cl-\overset{\overset{O}{\|}}{C}-Cl$$

Phosgene was used in World War I as a suffocating agent in warfare. Its effect is not noticed at first and symptoms of poisoning do not appear for the first two hours; it is more toxic than chlorine by about ten times. Although it is extremely dangerous to work with phosgene, the gas is used rather often in various laboratory syntheses and in industry.

CARBOXYLIC ANHYDRIDES

Important functional derivatives of acids are their anhydrides, which can be regarded as the products of acid dehydration

$$R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R+H_2O$$

or as acyl oxides $\left[R-\overset{\overset{O}{\|}}{C}-\right]_2O$.

In anhydride molecules, two acid radicals are linked through oxygen. Their names are composed on the basis of the names of the corresponding acids.

12.15. Preparation Methods. Properties. Anhydrides can be obtained by the reaction between acid chlorides and the salts of carboxylic acids. Mixed anhydrides are formed if the derivatives of different acids are taken:

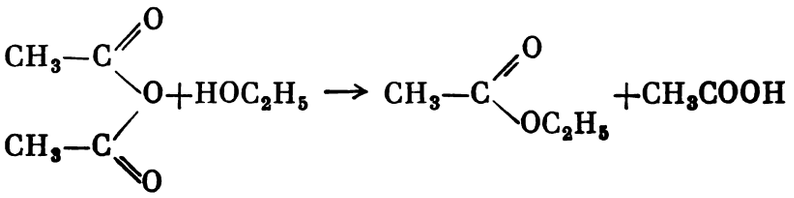
$$R-\overset{\overset{O}{\|}}{C}-Cl + NaO-\overset{\overset{O}{\|}}{C}-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'+NaCl$$

Anhydrides can be prepared also from ketene and carboxylic acids. This method is used industrially for producing acetic anhydride:

$$CH_2=C=O+CH_3-\overset{\overset{O}{\|}}{C}-OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

Anhydrides of lower acids are liquids with a pungent odour and are insoluble in water. Anhydrides of higher acids are crystalline substances without odour. The boiling points of anhydrides are higher than those of the corresponding acids.

Anhydrides are similar to acid chlorides by their chemical properties. They are also acylating agents, but reactions with them occur more mildly than with acid chlorides. *Esters* are obtained when anhydrides act on alcohols, and *amides*, when they act on ammonia. These reactions are quite similar to those of acid chlorides, but they result in the formation of a mixture of a basic product and an organic acid. For example, the reaction with alcohols occurs in the following way:

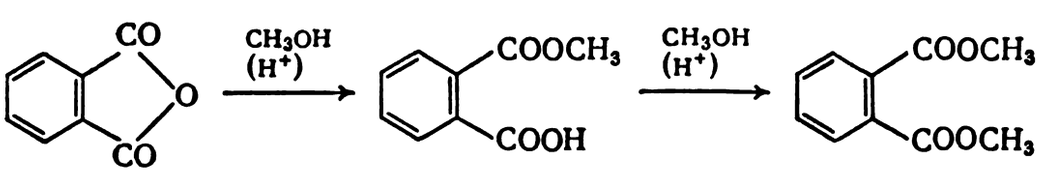


Anhydrides are hydrolyzed by water up to acids, but more slowly than acid chlorides.

12.16. Individual Representatives. *Acetic anhydride* is a liquid which boils at 140°C; it does not mix with water, and reacts only slowly with it in the cold. It is obtained industrially in large amounts from ketene and acetic acid. Large amounts of acetic anhydride are used for producing cellulose acetate fibers. Acetic anhydride is used as an acetylating agent.

Maleic anhydride is a crystalline substance which melts at 60°C. The methods of obtaining it have been discussed earlier (see Sec. 12.12). Maleic anhydride is a typical "dienophile" in reactions involving conjugated dienes (see Sec. 6.2). It is used for quantitatively determining butadiene in gases when synthetic rubber is being produced and for identifying other diene hydrocarbons, and in the plastics industry.

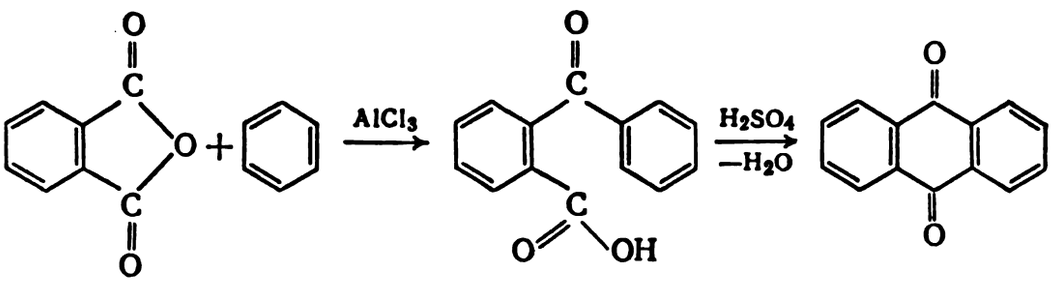
Phthalic anhydride is a crystalline substance which crystallizes as needles; its m.p. is 128°C, and b.p., 285°C, and it readily sublimes. Phthalic anhydride is obtained industrially by oxidizing naphthalene (see Sec. 7.10) and is used for various syntheses. It gives, with alcohols, monoesters and diesters of phthalic acid:



Dimethyl phthalate is a liquid having a faint odour; it is used as a *repellant* against mosquitoes, black flies, horseflies and ticks.

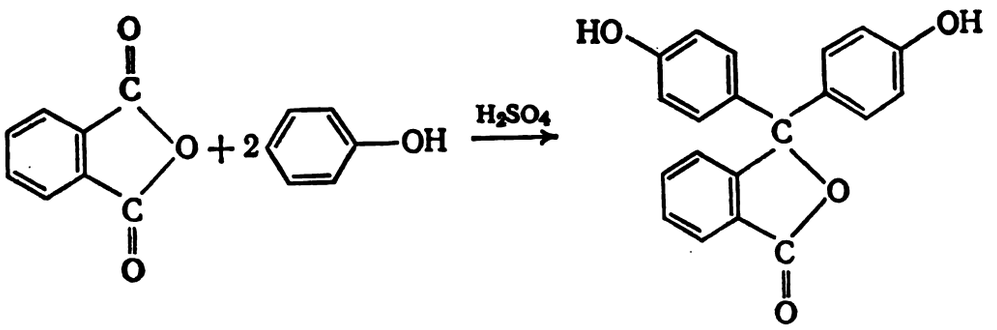
Some phthalic esters, e.g., *dibutyl phthalate*, are good plasticizers.

When phthalic anhydride interacts with ammonia, it forms *phthalimide* (see Sec. 12.23). Anthraquinone, which is widely used for producing dyes, is obtained when phthalic anhydride with benzene is condensed in the presence of aluminium chloride (industrial method):



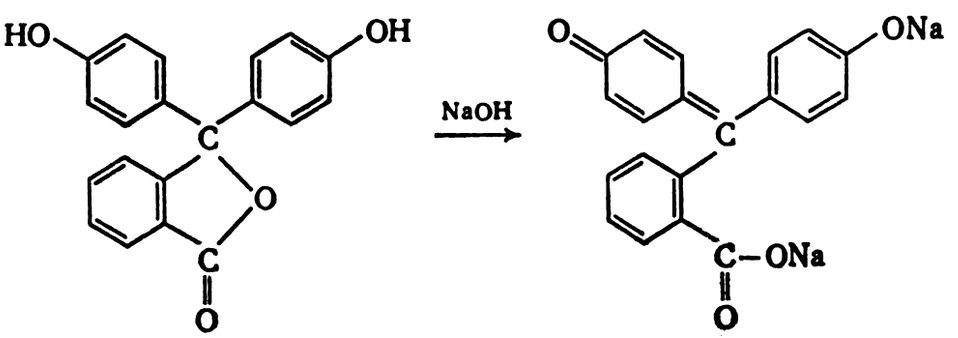
Phthalic anhydride | *o*-Benzoyl benzoic acid | Anthraquinone

Phthalic anhydride is characterized by reactions of condensation with phenols at the expense of the carbonyl oxygen. Such a reaction results in the formation of *phthaleins*, i.e., compounds which relate to triphenylmethane derivatives:



Phenolphthalein

Phenolphthalein is a white crystalline substance which dissolves well in alcohol. It passes over into a bright crimson salt under the action of alkalies:

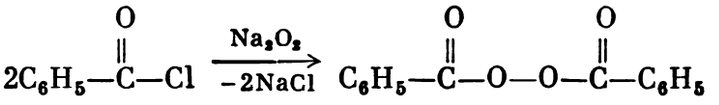


It is used as an indicator and, in medicine, as a weak laxative known as *purgen*. There are also other dyes of such a type. For example, *fluorescein* is formed in the condensation of phthalic anhydride with resorcinol.

Phthalic anhydride enters into a polycondensation reaction with monohydric alcohols, forming *alkyd resins* (see Sec. 23.9).

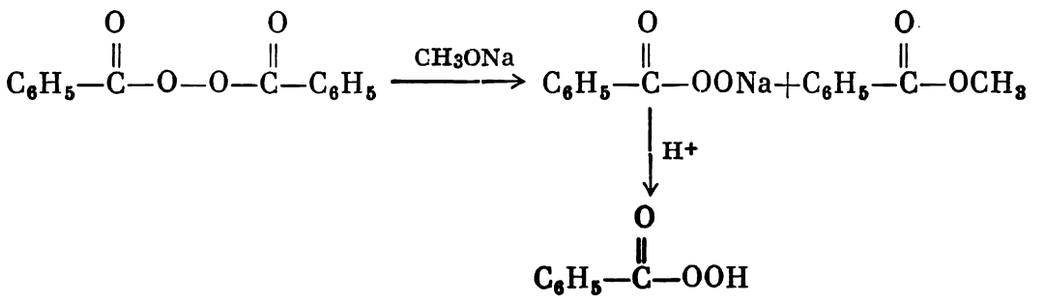
ACYL PEROXIDES. PERACIDS

12.17. Preparation Methods. Individual Representatives. Acyl peroxides are obtained when acid anhydrides or acid chlorides interact with metal peroxides:



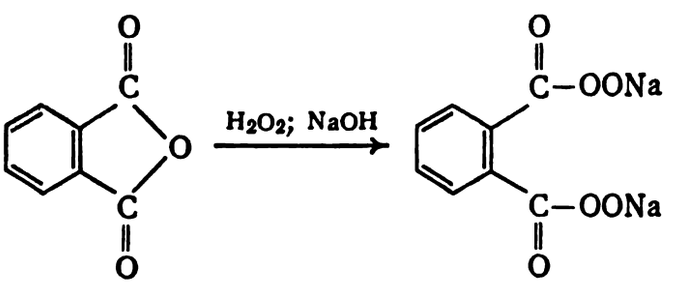
Benzoyl peroxide

Acyl *hydroperoxides* or *peracids* are obtained when acyl peroxides interact with sodium alkoxide followed by the action of a mineral acid:



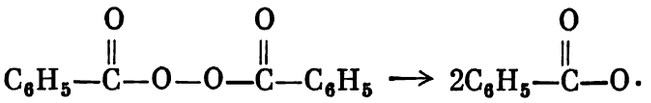
Perbenzoic acid

Peracid salts are obtained also by the reaction between anhydrides and hydrogen peroxide in the presence of caustic alkali:



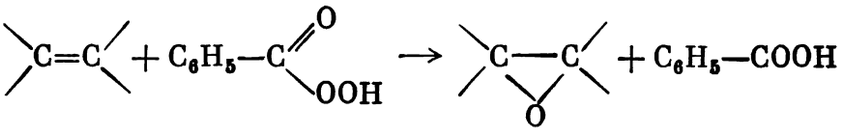
Acyl peroxides and peracids are strong oxidizing agents. Peracids slowly decompose in the cold, liberating oxygen, while they explode on heating, and therefore they cannot be distilled. Acting as oxidizing agents, they evolve halogen from hydrogen halides and oxidize alkenes to oxides. They are usually used as solutions in chloroform or carbon tetrachloride.

Benzoyl peroxide is a crystalline substance which melts at 108°C. It is more stable than other acyl peroxides. It can be stored and transported. It decomposes with an explosion when it is heated or when ultraviolet rays act on it. When a solution of peroxide in an organic solvent is heated, degradation slowly occurs and free radicals are formed:



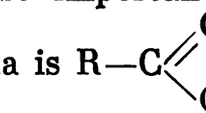
Benzoyl peroxide is used industrially as an initiator of polymerization.

Benzoyl hydroperoxide (*perbenzoic acid*) is a crystalline substance which melts at 43°C and has a hypochlorite odour. It is obtained from benzoyl peroxide and sodium alkoxide. Benzoyl hydroperoxide is used in synthesis and as a reagent for determining the position of the double bond (*Prilezhaev's reaction*). When it acts on olefins, α-oxides are formed:

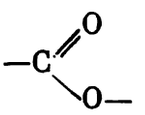


Glycols are formed when water acts on α-oxides, and ketones or aldehydes are formed when glycols are oxidized. The position of the double bond can thus be determined by the oxidation products.

CARBOXYLIC ESTERS

Esters are the most important functional derivatives of acids. Their general formula is  , i.e., they can be regarded as derivatives of acids in which the hydroxyl is replaced by the alkoxyl group.

12.18. Isomerism. Nomenclature. Physical Properties. The isomerism of esters is engendered by the structure of radicals attached to the *acylate* group



The names of esters are usually derived from the hydrocarbon radical of alcohol and the root of the Latin name of an acid with the addition of the suffix **ate** (or **oate** instead of the suffix **ic** in an acid). Names formed from those of alcohols and acids which yield ester are also used (Table 12.4).

TABLE 12.4. Examples of Names of Esters

Formula	Name	
	rational	in modern international nomenclature
$H-\overset{\overset{O}{\|}}{C}-OCH_3$	Methyl ester of formic acid	Methyl formate
$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$	Ethyl ester of acetic acid	Ethyl acetate
$CH_2=CH-CHCl-\overset{\overset{O}{\|}}{C}-OC_2H_5$	—	Ethyl-2-chloro-3-buten-oate

Esters are widely distributed naturally. The aroma of many flowers, fruits and berries is due to the presence of esters in them. *Fats* relating to esters are very wide-spread in the vegetable and animal kingdoms.

Esters of lower monohydric alcohols and lower acids are volatile liquids having a pleasant odour of flowers and fruits. Ethyl formate has the odour of rum; isoamyl acetate, that of pears; ethyl butyrate, apricots; isoamyl butyrate, pineapples; isoamyl isovalerate, apples; benzyl acetate, jasmine, and so forth. Owing to their odour, these esters are used as "fruit essences" in perfumery and the food industry. They dissolve poorly in water, but well in organic solvents, and are solvents themselves. The boiling points of esters are lower than those of the corresponding acids, because association is not their inherent feature. For example, the boiling point of acetic acid is 118°C, while that of ethyl acetate, 78°C.

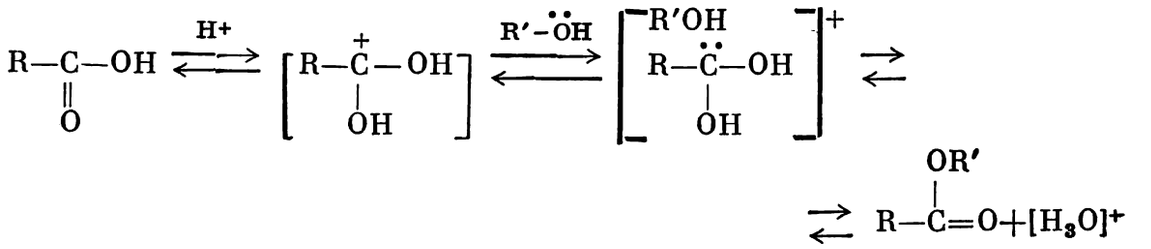
12.19. Preparation of Esters. A very important method of obtaining esters is the interaction between carboxylic acids and alcohols (*esterification reaction*):

$$R-\overset{\overset{O}{\|}}{C}-OH + R'-OH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

The catalysts used in this case are concentrated H_2SO_4, gaseous HCl, BF_3, etc.

The effect of an acid catalyst consists in the protonation of the carbonyl oxygen and, consequently, in an increase of the positive charge borne by the carbon atom of the carboxyl group, and this

makes it more capable of being added to the nucleophilic reagent, i.e., alcohol:

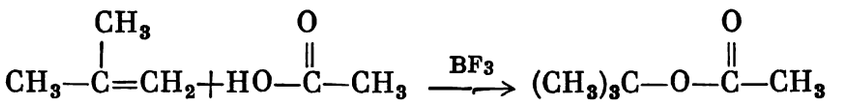


The fact that the oxygen atom of alcohol remains in the composition of ester was proven by means of alcohol lebelled with isotope ^{18}O.

The esterification reaction is reversible. An excess of alcohol or acid favours the shift of equilibrium to the right. The ester yield can be increased also by continuously removing one of the substances being formed (ester or water) from the reaction sphere.

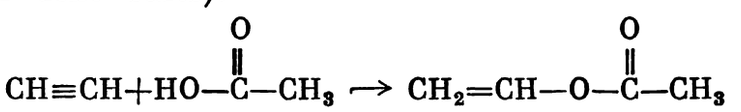
The esterification reaction rate depends on the nature of acid and alcohol, i.e., on the carbon atom with which the hydroxyl group (primary, secondary or tertiary) is linked and on the structure of the carbon chain which is attached to the carboxyl group. Bulky radicals create steric hindrances and impede the formation of intermediate addition products. Tertiary alcohols undergo esterification especially poorly (N. A. Menshutkin, 1887).

Other methods of obtaining esters include the acylation of alcohols by acid chlorides or anhydrides (this is how, for instance, esters of both tertiary alcohols and phenols are obtained) and the industrially important addition of carboxylic acids to alkenes:



tert-Butyl acetate

The addition of carboxylic acids to acetylene is also used industrially. This is how vinyl esters are obtained (200°C, in the presence of cadmium or zinc salts):

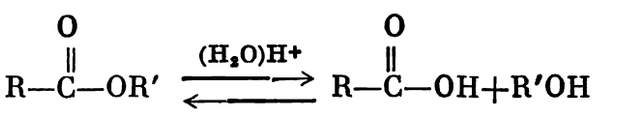


Vinyl acetate

Vinyl acetate is an important intermediate for polymer synthesis.

12.20. Chemical Properties. Esters are characterized by the following chemical reactions:

1. Action of water (*hydrolysis*). An acid or a basic medium promotes this reaction. If the reaction is catalyzed by acid, it is reversible and results in the formation of acid and alcohol:



In an alkaline medium, the reaction is irreversible and occurs more rapidly, as a result of which alcohol and an acid salt are formed.

The ability of esters to be hydrolyzed in an alkaline medium fundamentally distinguishes them from ethers and acetals. Acetals can be hydrolyzed only in an acid medium, while ethers are cleaved only under the action of strong hydrohalic acids.

2. Reaction of transesterification. *Alkoxy groups are exchanged* when esters with alcohols are heated in the presence of a mineral acid or an alkoxide (alkaline medium). The reaction is reversible and the degree of conversion depends on the amount of alcohol taken:

$$R-\overset{\overset{O}{\|}}{C}-OR'+R''OH \rightleftarrows R-\overset{\overset{O}{\|}}{C}-OR''+R'OH$$

The reaction is important in obtaining various esters.

3. The action of ammonia (*ammonolysis*) engenders acid amides:

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5}+NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2}+C_2H_5OH$$

4. Esters are reduced more readily than acids. As a result, primary alcohol which corresponds to an ester acid is obtained. The reducing agents used are lithium aluminium hydride, sodium in boiling alcohol or hydrogen in the presence of a copper-chromium catalyst:

$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow{\text{reduction}} R-CH_2OH+R'OH$$

5. Esters are stable towards the action of oxidizing agents. Therefore, in oxidation reactions, these groups are esterified beforehand to protect alcohol or phenol groups, and then they are hydrolyzed after oxidation.

12.21. Waxes. Natural waxes are a mixture of esters of higher fatty acids and higher alcohols that contains also free higher alcohols, free acids and paraffins with a normal chain of carbon atoms. Beeswax (m.p. 60-62°C) consists of esters of primary alcohols and acids having an even number of carbon atoms C_{24}-C_{34} and of free alkanes having an odd number of carbon atoms C_{25}-C_{31}.

Some plants secrete a protective film of wax on leaves and fruits. The composition of cotton wax is similar to that of beeswax. Wax on tobacco leaves consists almost only of paraffins C_{25}-C_{33}, while that on cabbage leaves is paraffin $C_{29}H_{60}$ by 95 per cent.

Solid wax, or *spermaceti* (m.p. 41-48°C), and liquid wax, or *sperm oil*, have been isolated from the head of the sperm whale. Spermaceti

consists mainly of cetyl palmitate (cetyl ester of palmitic acid), $C_{15}H_{31}COOC_{16}H_{33}$. The main constituent of sperm oil is esters of unsaturated alcohols (oleic alcohol, $C_{17}H_{33}CH_2OH$) and higher unsaturated acids having an even number of carbon atoms C_{12}-C_{16}.

Lanolin, or suint, is a mixture of esters of acids C_{10}-C_{20} and of alcohols C_{18}-C_{20} (hydroxy acids and other substances are also in its composition).

The density of wax and its solidification temperature depend on its composition (on the length of the radical chain and the degree of unsaturation). The longer the chain of carbon atoms of an acid or alcohol, the higher is the melting point. The presence of double bonds in the molecule brings down the melting point. Spermaceti and lanolin are used in medicine and perfumery for making various pastes and creams.

FATS AND FATTY SUBSTANCES

12.22. Natural Fats. Lipids. Fats and fatty substances, known by the common name of *lipids*, are in the composition of plant and animal organisms together with proteins and carbohydrates.

Lipids are in the organism either as protoplasmatic fat (they are in the composition of the cell protoplasm) or as reserve fat (they are in the composition of the fat tissue). Protoplasmatic fat as a cell constituent is in the organism in the form of complex compounds with a protein, and its amount does not change when the organism becomes emaciated from starvation or when it gets fat. In such cases, the amount of reserve fat changes.

Lipids are important biologically: they are the energy source for an animal organism, and 39 J are evolved when one gram of fat is oxidized in it. They are good solvents of biologically active substances (e.g., vitamins), which are needed by an animal organism to function normally. The fat tissue forms a soft insulating interlayer, protecting the inner organs and the entire body from jolts, impacts and supercooling.

The amount of fat which accumulates in an animal organism is dependent on the diet, age and other factors. It usually constitutes 10-20 per cent of the total mass of a human organism (it can be higher when pathological changes occur in the organism). The amount of fat reaches 50 per cent of the total mass of animals which are specially fed "for weight". In plants, vegetable oils accumulate usually in seeds and fruits (linseed, hempseed, sunflower seeds, olives, etc.) also up to 50 per cent of the total mass.

Plants synthesize fats from starch, which is the product of carbon dioxide assimilation. In the animal organism, fats are formed from food fats and are synthesized from food carbohydrates (meal and sweet dishes promote adiposity).

The main constituent of plant and animal fats is esters of glycerol with higher fatty acids: triglycerides of palmitic, stearic, oleic and linoleic acids, etc. The chemical nature of fats was ascertained in the first quarter of the nineteenth century by Chevreul. The first fat synthesis was effected by Berthelot (1854) by heating glycerol with stearic acid:

$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + 3HO{-}\overset{\overset{O}{\|}}{C}{-}C_{17}H_{35} \xrightarrow{200^\circ C} \begin{array}{l} CH_2{-}O{-}COC_{17}H_{35} \\ | \\ CH{-}O{-}COC_{17}H_{35} \\ | \\ CH_2{-}O{-}COC_{17}H_{35} \end{array} + 3H_2O$$

Tristearin

In all the fats, the alcohol residue is the same (glycerol residue): the difference between fats depends on acid residues.

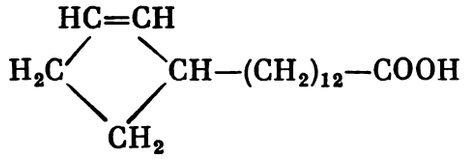
The most important acids in the composition of fats and fatty substances are monocarboxylic acids, which contain an even number of carbon atoms and an unbranched carbon chain. Saturated acids in fats include butyric (C_4), caproic (C_6), caprylic (C_8), capric (C_{10}), lauric (C_{12}), palmitic (C_{16}), stearic (C_{18}) and arachic (C_{20}) acids. Unsaturated acids in them include palmitoleic, oleic, linoleic and linolenic acids.

Oleic I, palmitic II and stearic III acids are most commonly found in fats. Chaulmoogric acid IV is found in small amounts in them.

$CH_3{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}COOH$ (I)

$CH_3{-}(CH_2)_{14}{-}COOH$ (II)

$CH_3{-}(CH_2)_{16}{-}COOH$ (III)



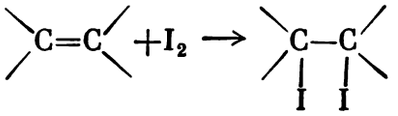
(IV)

The fats of oil-bearing fruits contain much unsaturated oleic acid (up to 80 per cent of olive oil and up to 36 per cent of sunflower oil). Human fat contains up to 70 per cent of oleic acid and up to 25 per cent of palmitic acid. The fats of ruminants contain much stearic acid. Milk fats contain up to 40 per cent of oleic acid and up to 25 per cent of palmitic acid; they are characterized also by the presence of lower saturated acids C_4-C_{12}. Cow butter contains up to 2.4 per cent of butyric acid, goat and sheep milk contains many acids C_6 and C_8, and the fats of sea mammals contain many unsaturated acids C_{16} and C_{18}.

A different acid composition engenders different physico-chemical and chemical properties of fats. Natural fats do not have a clearly defined melting point, because they are complex mixtures of glycerides; they melt in a definite temperature range, softening at

first. The solidification temperature of a fat is the higher, the greater is the amount of saturated acids (palmitic, stearic) in it.

The degree of unsaturation in fats is determined by the *iodine number* (known also as the "iodine value"), which shows the number of grams of iodine that well add to unsaturated components present in 100 g of a fat under specific conditions:



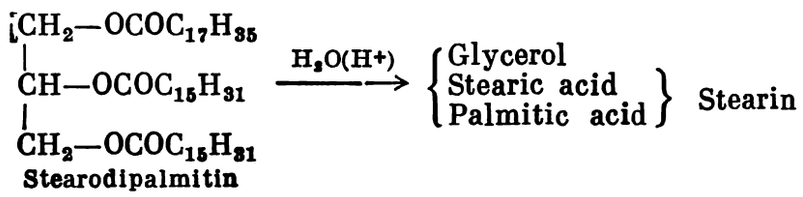
The iodine number of butter is 30; that of hempseed oil, 150, and that of linseed oil, 170-180.

Fats readily dissolve in organic solvents: ether, chloroform, carbon tetrachloride, benzene, toluene and gasoline. They are practically insoluble in water, but can form stable emulsions with it in the presence of surfactants. Fats are emulsified in the animal organism under natural conditions by such surfactants as proteins, bile salts, etc.

An example of an aqueous emulsion of fat stabilized by a protein is milk. Emulsification is needed for the digestive organs to rapidly digest food fats. In digestion, fats are hydrolyzed under the action of the lipase enzyme (which is in saliva, the liver, and gastric and intestinal juices) up to free acids and glycerol, which pass through the intestinal walls and are then bound again in different combinations, being deposited as reserve fat.

Fats turn rancid when exposed to moist air and light for any length of time, i.e., they acquire an unpleasant odour and taste, and their acidity increases. The acids C_6-C_{12}, and also methyl ketones, which are formed as a result of fat oxidation, have an unpleasant odour.

Industrial fat processing. In industry, the hydrolytic lipolysis reaction is widely used for obtaining glycerol and fatty acids or their salts, i.e., soaps. Lipolysis is effected in both acid and alkaline media. In the first case, glycerol and a mixture of free acids, stearin, are formed:



Stearodipalmitin

In an alkaline medium, the salts of these acids, *soaps*, are obtained together with glycerol.

Alkali or lime can be used for creating an alkaline medium. An acid catalyst is, for instance, *Petrov's contact*, which is a mixture of naphthenic acids, petrolatum oil, sulphuric acid and water.

A very important reaction used industrially is the *hydrogenation of fats*, i.e., the conversion of liquid fats into solid ones. This reaction consists in the addition of hydrogen to unsaturated fatty acids and their conversion into a saturated acid (Ni, 200°C, 15 kg/cm^2):

$$\begin{array}{l} CH_2{-}OCOC_{17}H_{33} \\ | \\ CH{-}OCOC_{17}H_{31} \\ | \\ CH_2{-}OCOC_{17}H_{29} \\ \text{Liquid fat} \end{array} \xrightarrow{+6H_2} \begin{array}{l} CH_2{-}OCOC_{17}H_{35} \\ | \\ CH{-}OCOC_{17}H_{35} \\ | \\ CH_2{-}OCOC_{17}H_{35} \\ \text{Solid fat} \end{array}$$

Vegetable oils, fish-liver oil, marine mammals fats having an unpleasant odour, and others are subjected to hydrogenation, as a result of which the dark colour and odour disappear.

Solid fats have an advantage over liquid ones, because they are more convenient to transport, and from them we may obtain stearin for candles, solid soap, etc. The best grades of hydrogenated fat are used for obtaining margarine.

Margarine is an emulsion of hydrogenated fat, animal fat (low-melting beef tallow) or vegetable oil in milk. It is similar to butter by its appearance and odour; egg yoke is added to the product in order to make it yellow, and the diketone called *diacetyl*, $CH_3COCOCH_3$, which is the principal aromatic ingredient of butter, is added to it for the sake of odour.

Vegetable oils are characterized by autooxidation and polymerization processes. These properties are used industrially for making drying oil, lacquers and paints. Drying oil is made from oils which contain a large amount of linoleic and linolenic acid esters. They include linseed, hempseed, sunflower and other oils. *Drying oil* is a dense dark liquid which "dries" in the air, forming a film. As it dries, oils are oxidized by atmospheric oxygen. To accelerate this process, *siccatives* (oxides or salts of cobalt, manganese or lead) are added to it.

The oxidized polymer of linseed oil is dense elastic oil known as *linoxyn*, which is used for making linoleum and oilcloth.

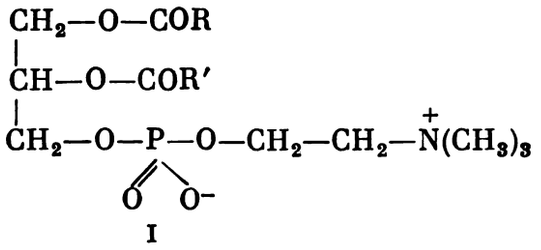
Mixtures of vegetable and mineral oils are used for producing some lubricants. Dense lubricants are made from animal fats. Fats are used also for pharmaceutical purposes and in perfumery (to make creams, pomades, etc.).

Lipids are fatty substances found in animal organisms and plants. Phosphatides are an important group of lipids found in the brain and nerve tissues.

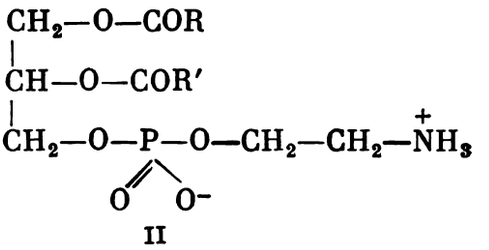
When *phosphatides* are hydrolyzed, they yield glycerol, fatty acids, phosphoric acid and amino alcohols. A distinction is made between *lecithins*, which contain a residue of the amino alcohol called choline, and *cephalins*, which contain a residue of ethanolami-

ne, depending on the residue of an alcohol which is in the composition of phosphatides.

In the lecithin molecule, unlike fats, one of the hydroxy groups of glycerol is bound not with a fatty acid, but with phosphoric acid as its ester with amino alcohol). The formulas of lecithin I and cephalin II are given below:

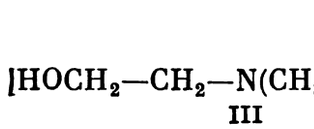


I

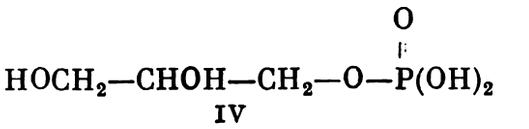


II

Lecithins are white waxy substances which dissolve in ether, alcohol and other organic solvents. They swell in water, and are in the composition of brain and nerve tissues and the egg yoke. In plants, they are found in seeds and sprouts. When lecithins are being hydrolyzed, free carboxylic acids, choline III and glycerophosphoric acid IV are formed:



III



IV

Cephalins are similar to lecithins by their structure, but their molecules contain an ethanolamine residue as a nitrogen base. When cephalins are being hydrolyzed, they yield carboxylic acids, glycerophosphoric acid and ethanolamine ($HO—CH_2—CH_2—NH_2$). Cephalins, together with lecithins, are found in tissues.

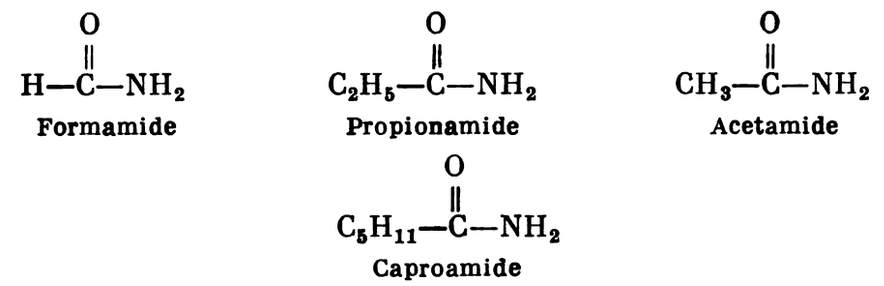
Lecithins and cephalins play a special role in cellular membranes, which are very important to the vital activity of cells.

Lecithins participate in the metabolism, absorption and transfer of fats and cholesterol. Conditions for the development of atherosclerosis are created when an organism lacks phospholipids.

ACID AMIDES

12.23. Preparation Methods. Properties. Amides are important functional derivatives of acids. They can be regarded as the products of substitution of the ammonia residue, the NH_2 group, for the hydroxyl group in the carboxyl. In amide molecules, the NH_2 group is linked with acyl; the general formula of amides is $R—\overset{\overset{O}{\|}}{C}—NH_2$.

Examples of amides and their names are given below:

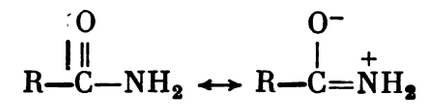


Compounds whose molecule contains the —NH— group attached to two acyl radicals are known as *imides.*

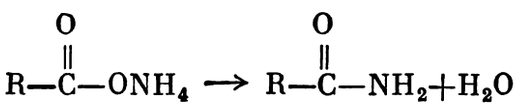
Some amides are liquids, while most of them are solids. Lower amides dissolve in water.

A study of interatomic distances has revealed that the lengths of the C=O and C—N bonds in amides are 0.124 nm and 0.132 nm, respectively, i.e., they differ from the lengths of the corresponding bonds in other compounds (see Table 1.2).

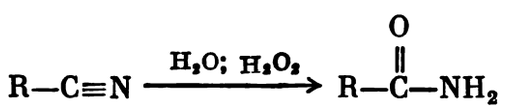
These and other structural features of amides indicate that their true structure is mesomeric and can be expressed by extreme formulas:



An important industrial method of preparing amides is by heating (dry distillation) ammonium salts of carboxylic acids:

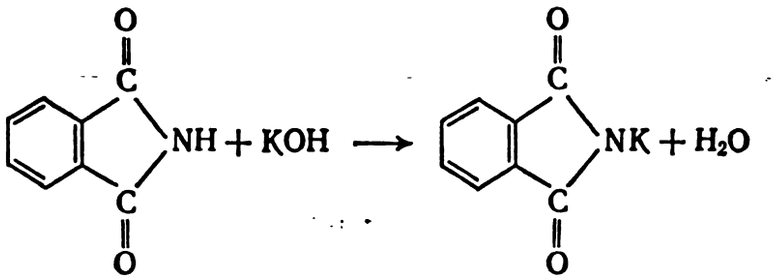


Amides are obtained when ammonia acts on the chlorides, anhydrides and esters of acids (Secs. 12.13 and 12.20). They are also formed when nitriles are partially hydrolyzed. Hydrolysis can be stopped at the amide stage, for instance, by adding hydrogen peroxide to a weakly alkaline medium:

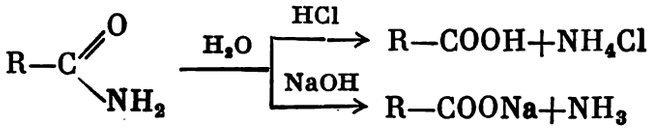


Amides, unlike ammonia, have almost no basic properties and they yield salts only with strong acids, such as $RCONH_2 \cdot HCl$, which are readily decomposed by water with the evolution of initial amide. When metallic sodium acts on amides in liquid ammonia, metallic derivatives of amides of the RCONHNa type are formed, thus revealing the acidic properties of amides. Cyclic amides (imides) are even more acidic. For example, phthalimide forms a potassium derivative, potassium phthalimide, when it is treated with

a caustic potash solution:



Amides, like other functional derivatives of acids, form acids when they are hydrolyzed in an acid or an alkaline medium:



Amides can be converted into acids also under the action of nitrous acid:

$$R{-}CONH_2 \xrightarrow{HONO} R{-}COOH + N_2 + H_2O$$

Nitriles are formed when amides with strong dehydrating agents (P_2O_5) are heated:

$$CH_3{-}CO{-}NH_2 \xrightarrow[-H_2O]{} CH_3{-}C{\equiv}N$$

Acetamide — Acetonitrile

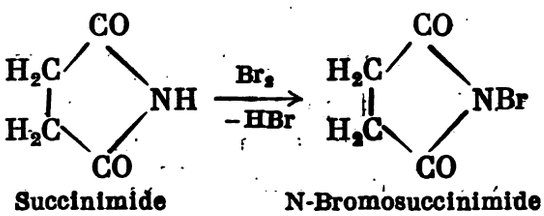
In the reduction of amides (lithium aluminium hydride or catalytic hydrogenation), primary amines with the same number of carbon atoms in the molecule are formed:

$$R{-}CO{-}NH_2 \xrightarrow{\text{reducing agent}} R{-}CH_2{-}NH_2$$

A peculiar reaction, known as the *Hofmann rearrangement*, occurs when sodium hypochlorite or hypobromite acts on amides in an aqueous alkaline solution. This reaction engenders *amines*, which contain one carbon atom less than the starting amides:

$$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + NaOCl + 2NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + NaCl + H_2O$$

Cyclic imides of dicarboxylic acids form N-halogen imides when they are carefully treated with chlorine or bromine in an alkaline medium:



Succinimide — N-Bromosuccinimide

N-Bromosuccinimide is a halogen "carrier" and is used as a brominating agent for putting bromine in the allylic position (see Sec.9.2).

12.24. Individual Amides. *Formamide*, $HCONH_2$, is a liquid whose b.p. is 193°C at 10 mm Hg, m.p., 2.5°C, d_4^{20}, 1.13. *Acetamide*, CH_3CONH_2, melts at 82°C and boils at 222°C, and it is obtained by subjecting ammonium salts of the corresponding acids to dry distillation.

Dimethylformamide is a liquid which boils at 150°C and mixes with water, ether and benzene. It is obtained in the reaction between dimethylamine and carbon monoxide under pressure in the presence of sodium methoxide:

$$(CH_3)_2NH + CO \xrightarrow{CH_3ONa} H-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$$

Formamide is obtained by a similar reaction between carbon monoxide and ammonia.

Formamide and dimethylformamide are used as solvents in the laboratory and for producing synthetic fibres in spinning.

Dimethylformamide is a selective solvent of some gases. It is used for isolating acetylene from gaseous mixtures (one part of dimethylformamide dissolves 31 parts of acetylene).

Carbamide (*diamide of carbonic acid, urea*) is a crystalline substance which melts at 133°C and is readily soluble in water, with greater difficulty in alcohol and is insoluble in ether and hydrocarbons.

Urea was first synthesized by Wöhler (1828) by heating potassium cyanate and ammonium sulphate:

$$KOCN \xrightarrow[-K_2SO_4]{(NH_4)_2SO_4} NH_4OCN \xrightarrow{100°C} H_2N-\overset{\overset{O}{\|}}{C}-NH_2$$

Urea is an end product of protein metabolism in mammals. When protein brakes down, about 80 per cent of nitrogen is excreted as urea. Human urine contains about 2 per cent of urea. Urea is an important commercial product which is obtained industrially in the following ways:

1. From carbon dioxide and ammonia on heating under pressure:

$$CO_2 + 2NH_3 \xrightarrow{200°C;\ 200\ kg/cm^2} H_2N-COONH_4 \xrightarrow[-H_2O]{} H_2N-CO-NH_2$$

2. From phosgene and ammonia:

$$Cl-\overset{\overset{O}{\|}}{C}-Cl + 4NH_3 \longrightarrow H_2N-CO-NH_2 + 2NH_4Cl$$

3. From cyanamide:

$$H_2N-CN + H_2O \longrightarrow H_2N-CO-NH_2$$

Urea is a weak base and forms salts with acids (1 equiv.). Its characteristic salt is mononitrate, $CO(NH_2)_2 \cdot HNO_3$, which is sparingly water-soluble and is used for isolating urea from a solution.

Urea has the ordinary properties of amide, i.e., it is hydrolyzed on heating in both acid and alkaline media and also under the action of nitrous acid:

$$H_2N—CO—NH_2+H_2O \longrightarrow CO_2+2NH_3$$

$$H_2N—CO—NH_2+2HNO_2 \longrightarrow CO_2+2N_2+3H_2O$$

When acylating agents act on urea, hydrogen of the NH_2 group is replaced by acyl, and then *ureides* are formed:

$$H_2N—CO—NH_2+(CH_3CO)_2O \longrightarrow H_2N—CO—NH—COCH_3+CH_3COOH$$

Ureides of some acids are used as medicinals (sedatives).

Urea is characterized by a reaction of condensation with formaldehyde. *Mono-* and *dimethylol ureas* are formed in a weakly alkaline solution:

$$H_2N—CO—NHCH_2OH \xleftarrow{CH_2O} H_2N—CO—NH_2 \xrightarrow{2CH_2O} HOCH_2NH—CO—NHCH_2OH$$

Methylol urea — Dimethylol urea

In a strongly alkaline or acid medium, these products are dehydrated and polymerized into high-molecular-weight resins known as *aminoplasts*.

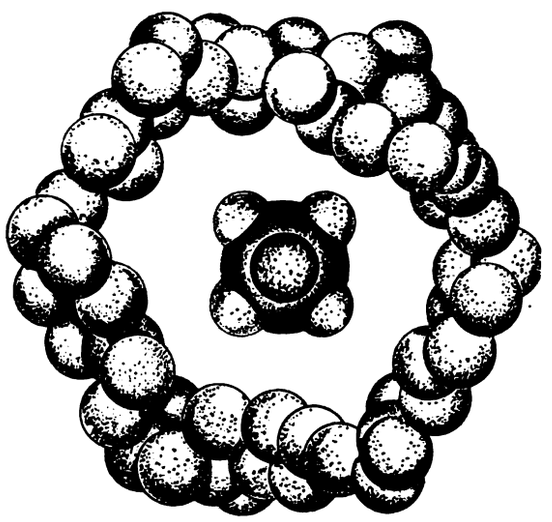


Fig. 12.4. Clathrate compound with urea

Urea is used industrially for obtaining polymers, medicinals and herbicides; it is a stabilizer of explosives, etc. In agriculture, it is used as a nitrogen-rich fertilizer and as a nonprotein feed supplement for sheep and cattle.

Inclusion compounds (*clathrates*). Urea crystals wetted with methyl alcohol are capable of taking up organic compounds (hydrocarbons, alcohols, halo alkanes, amines, etc.) only with a normal chain of carbon atoms, forming stable crystalline products.

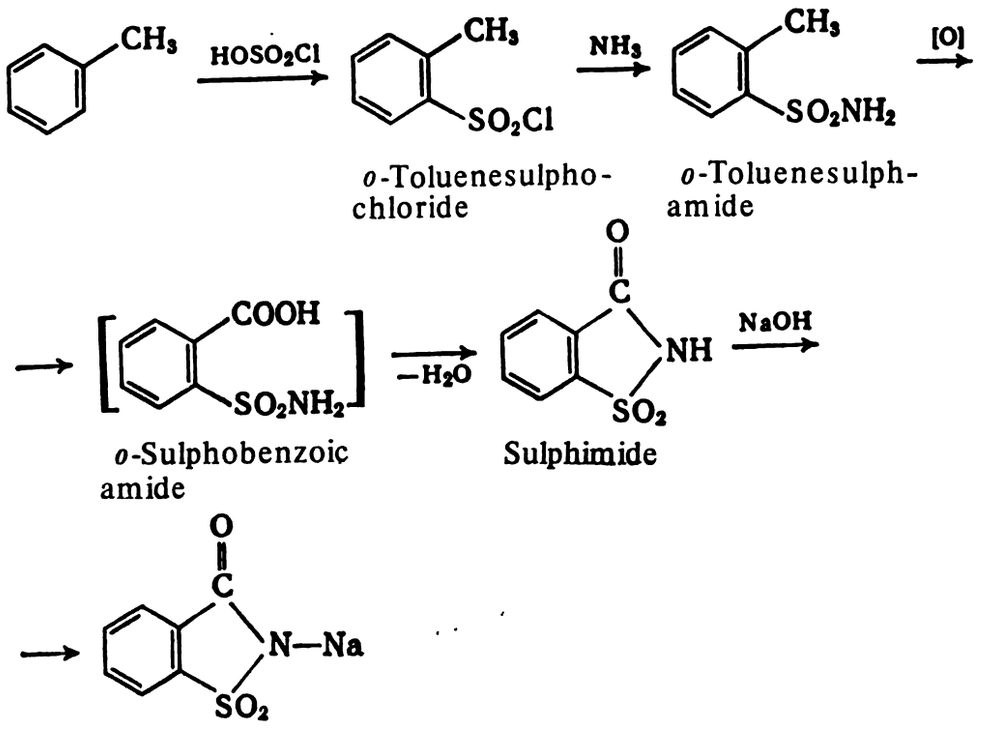
It has been ascertained that urea molecules are so oriented in a crystal lattice that hexahedral holes similar to honeycombs are formed between them. These holes may have molecules of unbranched compounds with at least seven carbon atoms (Fig. 12.4); branched molecules do not pass through. This makes it possible to separate

compounds with a normal carbon chain from branched-chain or cyclic compounds.

In the inclusion compounds formed, the "guest" molecules are not bound chemically with the "host" molecules, but are merely included in the holes formed by the crystal lattice. When crystals dissolve, the absorbed substances are isolated. Such compounds have become known as *inclusion compounds* or *clathrates* (from the Latin words "clat", meaning "bar", and "ratus", meaning "enclosed").

The ability of urea to yield clathrates is used in the oil-refining industry for improving the quality of fuel. Normal hydrocarbons, which reduce the octane number of fuel (they cause fuel detonation), are thus removed from gasoline. The solidification point of fuel for jet engines drops when *n*-alkanes are removed from it, because hydrocarbons having a branched chain melt at a considerably lower temperature.

Saccharin (*o-sulphobenzoic imide*) is obtained from toluene by the following scheme:



Saccharin is slightly soluble in water, but its sodium salt dissolves well in it. Saccharin is about 500 times sweater than sugar. This taste product is not assimilated by the organism and comes out unchanged with urine. It is not toxic and is recommended instead of sugar for diabetics. It can be used for making confectionery, fruit juice, etc.

ACID NITRILES

12.25. Preparation Methods. Properties. Nitriles (cyanides), R—C≡N, are derivatives of carboxylic acids, although they do not contain the acyl group. When nitriles are being hydrolyzed, the —C≡N group is converted into a carboxyl. Nitriles thus act in the same way as other functional derivatives of acids. The bond between nitriles and amides has already been discussed earlier. Nitriles can be regarded also as derivatives of hydrocyanic acid, H—C≡N, in which the hydrocarbon radical is substituted for hydrogen.

The names of nitriles are derived from the names of acids with the same number of carbon atoms; they are also called alkyl cyanides:

$CH_3—C≡N$	$CH_2=CH—C≡N$
Acetonitrile (methyl cyanide)	Acrylonitrile (vinyl cyanide)
$C_6H_5—C≡N$	$C_6H_5—CH_2—C≡N$
Benzonitrile (phenyl cyanide)	Phenylacetonitrile (benzyl cyanide)

Nitriles can be obtained by several methods:

1. By the action of potassium cyanide on alkyl halides. This method is interesting, because it causes the carbon chain to extend by one unit:

$$RBr + KCN \longrightarrow RCN + KBr$$

2. By heating acid amides (see Sec. 12.23) or aldoximes together with dehydrating agents:

$$\underset{\text{Benzaldoxime}}{C_6H_5CH=N—OH} \xrightarrow[-H_2O]{(CH_3CO)_2O} \underset{\text{Benzonitrile}}{C_6H_5—C≡N}$$

3. Aromatic nitriles are obtained by fusing sulphonates with potassium cyanide (see Sec. 13.3).

Nitriles are characterized by the hydrolysis reaction, which can occur both in acid and alkaline media:

$$R—C≡N \xrightarrow{2H_2O(H^+)} RCOO^- + NH_4^+$$

$$R—C≡N \xrightarrow{2H_2O(HO^-)} RCOONa + NH_3$$

When hydrolysis is carefully effected, at first amides, and then acids, are formed (see Sec. 12.23).

Primary amines are formed when nitriles are reduced. Sodium in alcohol, or lithium aluminium hydride can be used as a reducing agent, or catalytic hydrogenation can be effected:

$$R—C≡N \xrightarrow{4H} R—CH_2—NH_2$$

Hydrogen atoms attached to α-carbon in the nitrile molecule are mobile, because the —C≡N group is a strong electron acceptor.

It is similar to the carbonyl group in this respect. Both groups have a similar effect on α-hydrogen atoms, because the carbonyl group as well as the nitrile group bear a considerably high positive charge on the carbon atom:

$$\overset{\delta+\ \delta-}{-C\equiv N}$$

Particular mobility is possessed by hydrogen atoms attached to carbon which is linked with two nitrile groups, such as in malonodinitrile $NC-CH_2-CN$, or with one nitrile group and one phenyl group, such as in phenyl acetonitrile $C_6H_5-CH_2-CN$. Such compounds form sodium derivatives and are then alkylated:

$$C_6H_5-\underset{\underset{CN}{|}}{CH_2} \xrightarrow{C_6H_5ONa} C_6H_5-\underset{\underset{CN}{|}}{CHNa} \xrightarrow{C_2H_5I} C_6H_5-\underset{\underset{CN}{|}}{CH}-C_2H_5$$

These compounds readily enter into a reaction of condensation with aldehydes at the expense of α-hydrogen. These properties are used for various syntheses.

12.26. Individual Nitriles. *Acetonitrile* is a liquid which boils at 82°C and mixes with water in all proportions. It is a good solvent for many inorganic salts. Acetonitrile is obtained when dehydrating agents act on acetamide (see Sec. 12.23). It is now widely used industrially as a solvent, e.g., for removing resins and phenols from petroleum hydrocarbons. Acetonitrile, like other nitriles, is rather toxic, although it is not so dangerous as free hydrocyanic acid.

Acrylonitrile is a liquid which boils at 78°C and dissolves in water. It is prepared industrially by several methods:

1. From ethylene oxide and hydrocyanic acid under a pressure of 2.5 kg/cm²:

$$H_2C\!-\!CH_2 \xrightarrow{HCN;\ 60°C} \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{CN}{|}}{CH_2} \xrightarrow[-H_2O]{170°C} CH_2=CH-CN$$

Ethylene cyanohydrin

2. From acetylene and hydrocyanic acid (see Sec. 5.4).

3. By the oxidative ammonolysis of propylene in the presence of a cobalt-molybdenum catalyst:

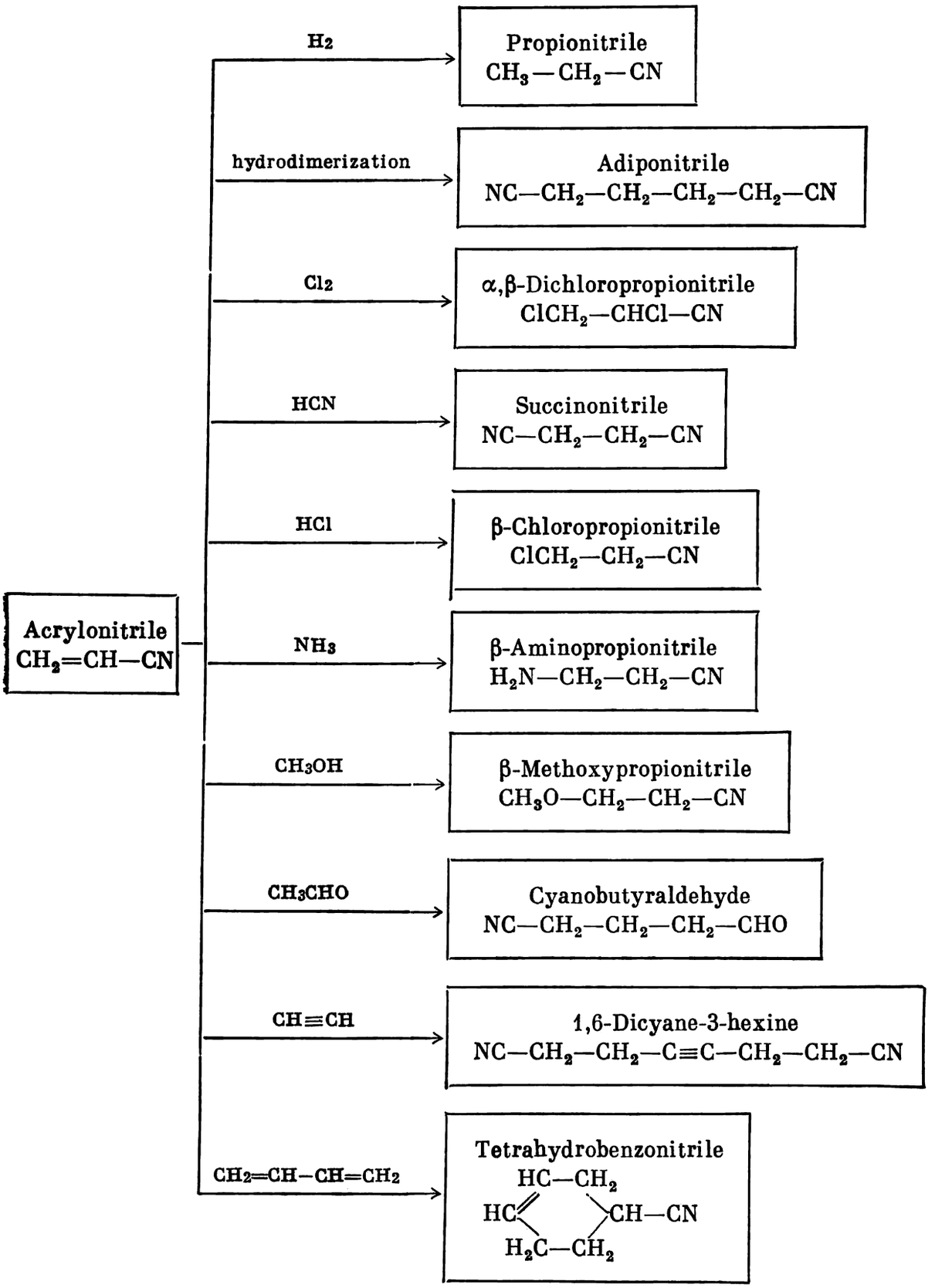
$$CH_2=CH-CH_3+NH_3+{}^3/_2O_2 \xrightarrow{450°C} CH_2=CH-CN+3H_2O$$

Acetonitrile is formed as a by-product (up to 10 per cent) in this reaction.

Acrylonitrile is very active chemically. It enters into the *cyanoethylation reaction* with many substances (hydrogenhalides, hydrogen cyanide, alcohols, amines, ammonia) according to the scheme:

$$HX+CH_2=CH-C\equiv N \longrightarrow X-CH_2-CH_2-C\equiv N$$

DIAGRAM 12.1. Industrial Use of Acrylonitrile



Markovnikov's rule seems to be violated, because the double bond is polarized under the action of the nitrile group:

$$\overset{\delta+}{C}H_2=\overset{\delta-}{C}H-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$$

Substances containing a mobile hydrogen atom attached to carbon, i.e., aldehydes, ketones, nitro compounds and malonic ester, also enter into the cyanoethylation reaction.

Acrylonitrile is widely used in laboratory and industrial syntheses because of the various opportunities offered by cyanoethylation reactions (see Diagram 12.1)

Acrylonitrile is used also as a monomer for producing synthetic rubber and synthetic fibres.

Chapter 13

ORGANIC SULPHUR COMPOUNDS

Sulphur and oxygen, being elements of the same group of the periodic system, are similar to one another in the formation of not only inorganic, but also organic compounds. However, unlike oxygen, sulphur in organic compounds can have different valencies.

Typical organic sulphur compounds are given in Table 13.1.

TABLE 13.1. **Types of Organic Sulphur Compounds**

Names	Sulphur compounds	Oxygen-containing analogues
Thiols (mercaptans)	R—SH	R—OH
Sulphides (thioethers)	R—S—R′	R—O—R′
Disulphides	R—S—S—R	R—O—O—R
Thioketones	R—C(=S)—R′	R—C(=O)—R′
Sulphenic acids	R—S—OH	
Sulphinic acids	R—S(=O)—OH	
Sulphonic acids (sulpho acids)	R—S(=O)(=O)—OH	
Sulphoxides	R—S(=O)—R	
Sulphones	R—S(=O)(=O)—R	
Sulphonates	$R_3\overset{+}{S}\ X^-$	

13.1. Thiols. Disulphides. Thiols (thioalcohols, mercaptans), R—SH, are monosubstituted organic derivatives of hydrogen sulphide. They can also be regarded as sulphur analogues of alcohols. The names of these compounds are formed by adding the suffix **thiol** to a hydrocarbon name, e.g., methanethiol (methyl mercaptan).

Thiols, like hydrogen sulphide, have a peculiar and a very obtrusive odour, which is stronger and more unpleasant than that of hydrogen sulphide. For lower thiols, the odour is sensed when the concentration is one part per 400 million parts of air. Negligible amounts of isopentanethiol are added to household gas to warn of leaks or escaping gas.

Thiols and their derivatives are found in the animal and vegetable kingdoms, e.g., propanethiol, C_3H_7SH, is found in freshly sliced onion, and butanethiol, C_4H_9SH, in skunk secretions. Sulphur is in the composition of some protein amino acids (see Sec. 22.1) and enzymes (see Sec. 22.6).

Thiols and hydrogen sulphide, unlike alcohols and water, are not associated, because sulphur does not form hydrogen bonds. Therefore, thiols are considerably less water-soluble than alcohols, and they boil at considerably lower temperatures:

	B. p., °C		B. p., °C
H_2O	100	H_2S	—61
CH_3OH	64.7	CH_3SH	7.6
C_2H_5OH	78.3	C_2H_5SH	34.7

Thiols can be obtained by the following methods:

1. By the reaction between alkyl halides and sodium hydrosulphide:

$$C_2H_5Br+NaSH \longrightarrow C_2H_5SH+NaBr$$

2. By passing vapours of alcohols and hydrogen sulphide over a heated catalyst (thorium oxide, 450°C):

$$ROH+H_2S \longrightarrow RSH+H_2O$$

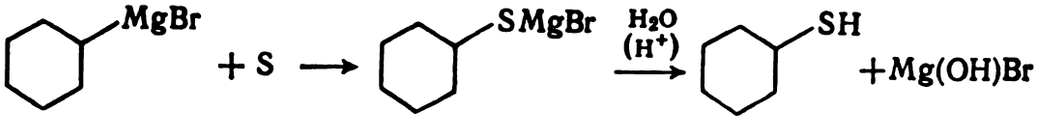
3. By the interaction between alkenes and hydrogen sulphide in an acid medium:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2+H_2S \xrightarrow{H_2SO_4} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-SH$$

4. From thiourea and alkyl halides in an alkaline medium:

$$RCl+S=C\begin{matrix}\diagup NH_2\\ \\ \diagdown NH_2\end{matrix}+3NaOH \longrightarrow RSH+2NH_3+Na_2CO_3+NaCl$$

5. By the action of sulphur on Grignard's reagent:



Cyclohexyl magnesium bromide

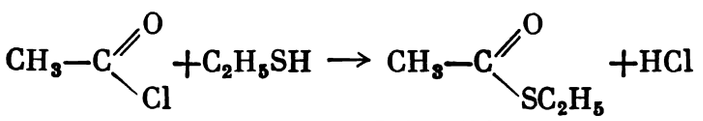
Cyclohexanethiol

6. Thiophenols are obtained from aromatic diazo compounds (see Sec. 16.2).

Thiols are similar to hydrogen sulphide by their chemical properties. Their acidic properties are more pronounced than those of the corresponding alcohols: they dissolve in aqueous alkaline solutions, forming salts called *mercaptides*, R—SNa. They form, with heavy metals, insoluble mercaptides. Mercury mercaptides are indicative in this respect:

$$2CH_3SH + HgO \longrightarrow (CH_3S)_2Hg + H_2O$$

Thiols, like alcohols, react with acyl chlorides, forming ester thioanalogues:



Ethyl thioacetate

Thiols and alcohols act differently towards oxidation. When alcohols are being oxidized, it is carbon and not oxygen which becomes oxidized to a greater extent. When thiols are being oxidized, the first to be oxidized is sulphur. *Disulphides* are formed under mild conditions:

$$C_2H_5—SH + O + HS—C_2H_5 \longrightarrow \underset{\text{Diethyl disulphide}}{C_2H_5—S—S—C_2H_5} + H_2O$$

The vigorous oxidation of nitric acid engenders sulphonic acids:

$$CH_3—SH \xrightarrow{3O} \underset{\substack{\text{Methane-}\\\text{sulphonic acid}}}{CH_3—SO_2OH}$$

13.2. Thioethers. Sulphoxides. Sulphones. *Thioethers* (dialkyl sulphides), R—S—R, are disubstituted organic derivatives of hydrogen sulphide. They can be obtained by the reaction between alkyl halides and sulphides or mercaptides of alkali metals:

$$2CH_3I + Na_2S \longrightarrow CH_3—S—CH_3 + 2NaI$$

$$C_2H_5Br + C_2H_5SNa \longrightarrow C_2H_5—S—C_2H_5 + NaBr$$

Thioethers are neutral liquids which boil at a higher temperature than the corresponding thiols.

They are readily oxidized (H_2O_2, CH_3COOOH) with the formation of *sulphoxides* and *sulphones*:

$$CH_3-S-CH_3 \xrightarrow[25°C]{[O]} CH_3-\overset{\overset{O}{\|}}{S}-CH_3 \xrightarrow{[O]} CH_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_3$$

Dimethyl sulphoxide (b.p. 86°C)

Dimethyl sulphone (b.p. 238°C; m.p. 110°C)

A representative of dialkyl sulphides is β,β′-*dichlorodiethyl sulphide* (*yperite*)

$$ClCH_2-CH_2-S-CH_2-CH_2Cl$$

which was used in World War I as a vesicant.

Diallyl disulphide, $CH_2=CH-CH_2-S-S-CH_2-CH=CH_2$, boils at 117°C (16 mm Hg). It is contained in garlic. Hence the name of the allyl radical (from the Latin words "allium sativum", meaning "garlic"). The antibiotic called *allicin*, or diallyl disulphide monosulphoxide, is obtained from garlic. Its formula is:

$$CH_2=CH-CH_2-\overset{\overset{O}{\|}}{S}-S-CH_2-CH=CH_2$$

13.3. Sulphonic Acids. Sulphochlorides. *Sulphonic acids*, or *sulpho acids*, are organic compounds whose molecule contains the sulpho group $-SO_3H$ (sulphuric acid residue), which is bound through sulphur with the hydrocarbon radical.

It has already been noted that *aliphatic sulphonic acids* can be obtained when thiols are vigorously oxidized and when halogen derivatives react with sodium sulphite:

$$C_2H_5I+Na_2SO_3 \longrightarrow \underset{\text{Sodium ethyl sulphonate}}{C_2H_5SO_3Na}+NaI$$

Free sulphonic acids can be isolated from salts under the action of mineral acids.

An industrially important reaction is the photochemical sulphochlorination of alkanes or cycloalkanes:

$$RH+SO_2+Cl_2 \longrightarrow RSO_2Cl+HCl$$

By its mechanism, it is a chain free-radical reaction (see Sec. 2.6).

In hydrolysis, the *sulphochlorides* obtained form sulphonic acids:

$$RSO_2Cl+H_2O \longrightarrow RSO_2OH+HCl$$

The salts called *alkyl sulphonates* are readily formed when alkalies act on sulphochlorides or free sulphonic acids:

$$RSO_2Cl + 2NaOH \longrightarrow RSO_2ONa + NaCl + H_2O$$
$$RSO_2OH + NaOH \longrightarrow RSO_2ONa + H_2O$$

It has already been noted (see Sec. 12.6) that alkyl sulphonates are good detergents which have an advantage over sodium carboxylates.

Aromatic sulphonic acids are obtained by directly sulphonating aromatic hydrocarbons by sulphuric acid. The sulphonation reaction is among the characteristic reactions of electrophilic substitution with respect to aromatic compounds. Concentrated sulphuric acid (*d* 1.84) or oleum is used for sulphonation. Di- and trisulphonic acids are obtained under more rigid conditions (300°C, greater SO_3 content in oleum).

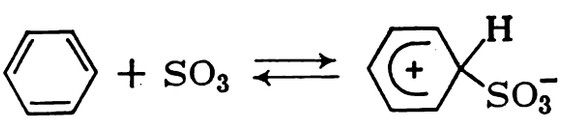
Different opinions are expressed on the sulphonation reaction mechanism. It is believed that under sulphonation reaction conditions (absence of water or its low content), the molecules of sulphuric acid, while interacting with one another, form active electrophilic particles, i.e., sulphur trioxide and the bisulphonium ion:

$$2H_2SO_4 \rightleftarrows \underset{\text{Sulphur trioxide}}{SO_3} + H_3O^+ + HSO_4^-$$

$$3H_2SO_4 \rightleftarrows \underset{\text{Bisulphonium ion}}{HSO_3^+} + H_3O^+ + 2HSO_4^-$$

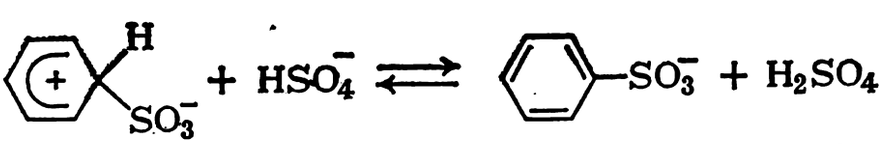
In these particles, the electron density on the sulphur atom is greatly reduced under the action of oxygen atoms, and therefore the sulphur atom is highly electrophilic.

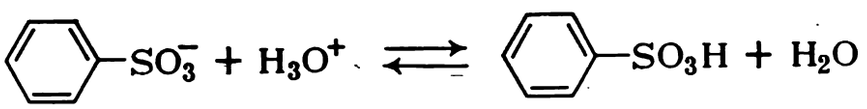
The first step of the sulphonation reaction, while occurring slowly, engenders the carbonium ion (σ-complex):



Carbonium ion

The second step occurs rapidly:





Equilibrium is greatly shifted to the left, because sulphonic acids in aqueous solutions are in the ionized state. They are strong acids, and their strength is comparable with mineral acids. The reversibility of the sulphonation reaction (see Sec. 7.5) is of practical importance.

After the reaction is completed, the mixture of sulphonic acids and sulphuric acid is diluted with a large amount of water (until complete dissolution is attained) and neutralized by the carbonate of calcium or barium. The sulphates of these metals precipitate, while calcium or barium sulphonates, from which free sulphonic acids can be isolated, remain in the solution.

Chlorosulphonic acid, $HOSO_2Cl$, can also be used as a sulphonating agent if it is employed in equimolar amounts:

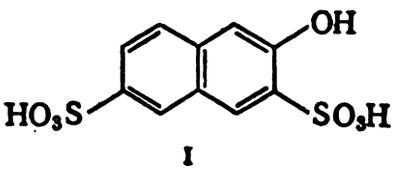
$$C_6H_6+HOSO_2Cl \longrightarrow C_6H_5SO_3H+HCl$$

Excess chlorosulphonic acid reacts with the sulphonic acid formed, yielding *sulphochlorides*:

$$C_6H_5SO_3H+HOSO_2Cl \longrightarrow \underset{\text{Sulpho-chloride}}{C_6H_5SO_2Cl}+H_2SO_4$$

Aromatic sulphonic acids are crystalline hygroscopic substances which are easily soluble in water. The sulpho group is often introduced into the molecule of an organic compound to make it more water-soluble. This is of great practical importance in dye production.

Sulphonic acids of naphthols, especially β-naphthol, are widely used in organic dye production. The most important of them are 2-naphthol-3,6-disulphonic acid (P-acid) I and dihydroxynaphthalene disulphonic acid, known as *chromotropic acid* II:



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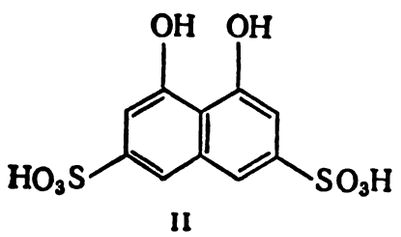


II

Dyes, which are obtained with the participation of chromotropic acid, produce different colours when they come into contact with various mordants.

The sulpho group is readily replaced by other groups, and therefore sulphonic acids are important intermediate products for syntheses. Their most important transformations are given below.

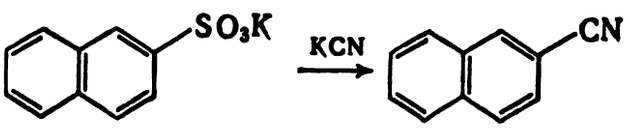
1. Sulphonic acids are subjected to hydrolysis by superheated water vapour in an acid medium; in this case, an aromatic compound

is regenerated and sulphuric acid is isolated (*desulphonation reaction*):

$$C_6H_5—SO_3H \xrightarrow[180°C]{H_2O\ (vapour);} C_6H_6+H_2SO_4$$

2. Phenols are formed when the hydroxyl group is substituted for the sulpho group (reaction of the alkali fusion of sulphonates, Sec. 10.8).

3. Nitriles are formed when sulphonates are fused with potassium cyanide:



β-Naphthonitrile

4. Sulphochlorides are formed when sulphonates are treated with phosphorus pentachloride:

$$C_6H_5SO_2ONa+PCl_5 \longrightarrow C_6H_5—SO_2Cl+POCl_3+NaCl$$

Aromatic sulphochlorides can be obtained by directly sulphochlorinating aromatic hydrocarbons by chlorosulphonic acid (excess):

$$C_6H_5—CH_3 \xrightarrow{HOSO_2Cl} CH_3—C_6H_4—SO_2Cl$$

Toluenesulphochloride

They are very reactive substances. For instance, they readily react with alcohols and phenols, forming sulphonate esters, which are good alkylating agents:

$$C_6H_5—SO_2Cl+HOCH_3 \longrightarrow C_6H_5—SO_2—OCH_3+HCl$$

Methyl benzenesulphonate

$$C_6H_5—SO_2Cl+HOC_6H_5 \longrightarrow C_6H_5—SO_2—OC_6H_5+HCl$$

Phenyl benzenesulphonate

They readily form, with ammonia, *sulphamides* (sulphonamides):

$$C_6H_5—SO_2Cl+2H—NH_2 \longrightarrow C_6H_5—SO_2—NH_2+NH_4Cl$$

Many sulphamide derivatives are medicinals and disinfectants (see Sec. 15.5).

Chapter 14

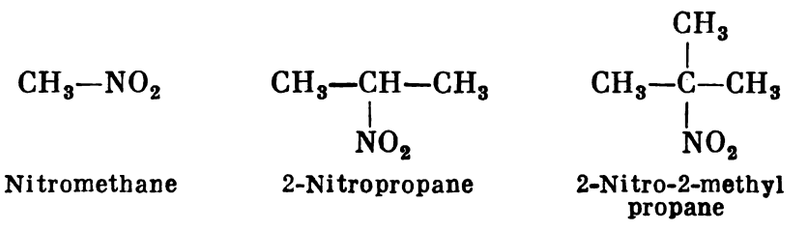
NITRO COMPOUNDS

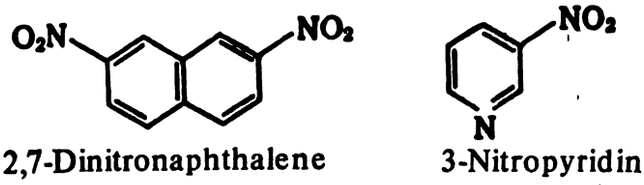
Nitro compounds are organic substances which contain the nitro group NO_2 as a functional group. The nitrogen atom of a nitro group is directly united to carbon, unlike nitrito compounds (nitrites), which contain the functional group ONO, where the bond is effected through oxygen. Nitrites are isomers of nitro compounds:

$R—NO_2$	$R—O—NO$
Nitro compound	Nitrite

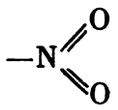
14.1. Isomerism. Nomenclature. Structure. Nitro compounds may be aliphatic (saturated or unsaturated), alicyclic, aromatic and heterocyclic, depending on the nature of an organic radical with which a nitro group is linked. Nitro compounds are subdivided into *primary*, *secondary* and *tertiary* ones (like halogen derivatives and alcohols) according to the nature of the carbon atom which is attached to a nitro group. A molecule can have one or several nitro groups. The prefix *nitro* is used in the names of nitro compounds, and it is placed in front of the name.

Formulas and names of different types of nitro compounds are given below:





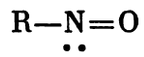
Structure. The electron configuration of the nitrogen atom is expressed by the scheme $1s^2 2s^2 2p^3$, i.e., the nitrogen atom has five valence electrons in the outer layer. Nitric acid, whose organic derivatives are nitro compounds, is, in inorganic chemistry, among the compounds having pentavalent nitrogen. Proceeding from this, the structure



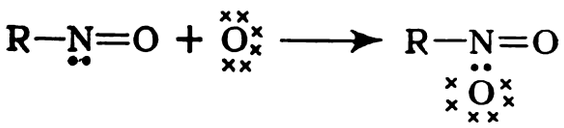
should be ascribed to the nitro group. When each nitrogen bond is replaced by an electron pair in such a formula, a *ten-electron* grouping will apparently be obtained around nitrogen, and this contradicts the octet rule.*

We may suppose the nitro group to have a different electron structure which does not violate the octet rule.

For this purpose, let us first consider the structure of *nitroso compounds*, in which nitrogen is in a trivalent state and has a free electron pair:



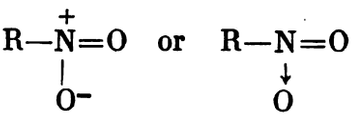
Nitrogen of the —NO group is capable of adding different atoms and groups at the expense of the free electron pair. When nitroso compounds add oxygen, they become nitro compounds:



In this case, oxygen was added, as it were, at the expense of another agent, i.e., the bonding electron pair belonged to the nitrogen atom. As a result, stable electron octets were formed for all the atoms in the composition of the nitro group. The nitrogen atom, which gave its free electron pair for the formation of a bond with oxygen, "lost", as it were, an electron (the free pair which belonged formerly to nitrogen has now been divided between nitrogen and oxygen), while oxygen gained an electron (one electron from a pair which oxygen shares with nitrogen). Consequently, nitrogen gained a positive charge equal to the electron charge, while oxygen, a corresponding negative charge. Nitrogen and oxygen are bonded, besides by an ordinary covalent bond, through an electron pair (only the origin of this pair is unusual), also by an electrovalent bond, through opposite charges.

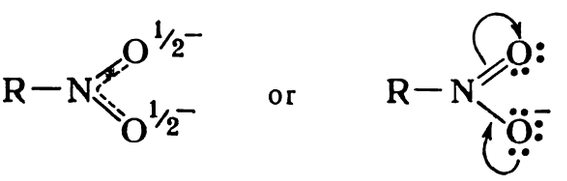
* "Octet expansion" is assumed to be possible for elements of the third and higher periods of the periodic table (phosphorus, arsenic, sulphur, etc.), but there is no reason to make such an assumption for elements of the second period, which has nitrogen.

Such a bond, being very common in nitrogen compounds, is known as the *coordination, semipolar* or *donor-acceptor* bond. The atom which donates its electrons for the formation of such a bond is called a *donor* (it is charged positively), and the atom which accepts electrons for filling up its octet and becomes negatively charged, an *acceptor*. Various formulas are used to denote such a type of bond in nitro compounds:

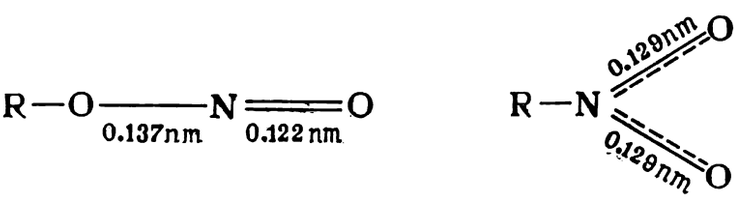


In the first case, charges originating on the atoms are indicated, and, in the second, the direction of the electron transfer is shown.

But the foregoing formulas, which obey the octet rule, likewise do not quite accurately express the true structure of a nitro group. *Mesomerism* is exhibited in this structure, i.e., the bonds have an intermediate nature and the distribution of electron density is equalized. Therefore, the following formulas show the structure of a nitro group more accurately:

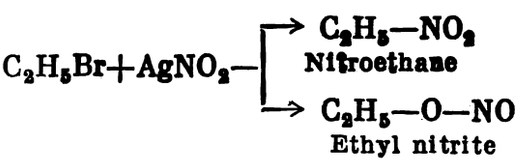


The mesomeric structure of the nitro group is confirmed by X-ray analyses: both N—O bonds have the same length which is intermediate between the length of the single bond N—O and that of the double bond N=O:



By its structure, the nitro group is similar to the carboxylate anion, which was considered earlier (see p. 253) and which is characterized by the same mesomerism.

14.2. Preparation of Nitro Compounds. 1. Nitro compounds can be obtained as a result of an exchange reaction between halogen derivatives and silver nitrite. Isomeric nitrites are always formed as by-products:



2. The main method of obtaining nitro compounds is the *nitration reaction*, i.e., the substitution of the nitro group for hydrogen:

$$R—H \longrightarrow R—NO_2$$

To effect nitration, use is made of various nitrating agents: a mixture of nitric and sulphuric acids (nitrating mixture), nitrates mixed with sulphuric acid, nitrogen oxides, etc.

The most diverse organic compounds, such as paraffin hydrocarbons, cycloparaffins and arenes and heterocycles, and also many substances (especially in the aromatic series) which already contain other substituents in the molecule, can be subject to nitration. Nitration is one of the most important transformations in organic chemistry, because nitration reactions are widely used and the products thus obtained are valuable.

Paraffins and cycloparaffins are nitrated by dilute nitric acid (*Konovalov's reaction*, p. 64) or by nitrogen oxides while heating them in a liquid or in vapour. This reaction occurs in accordance with the radical mechanism. According to A. I. Titov's concepts, the alkyl radical originates at the initial stage as the hydrogen atom is abstracted by nitrogen dioxide, oxygen or other initiators:

$$R—H + \cdot NO_2 \longrightarrow R\cdot + HNO_2$$

The radical formed interacts with the second molecule of nitrogen dioxide:

$$R\cdot + \cdot NO_2 \longrightarrow R—NO_2$$

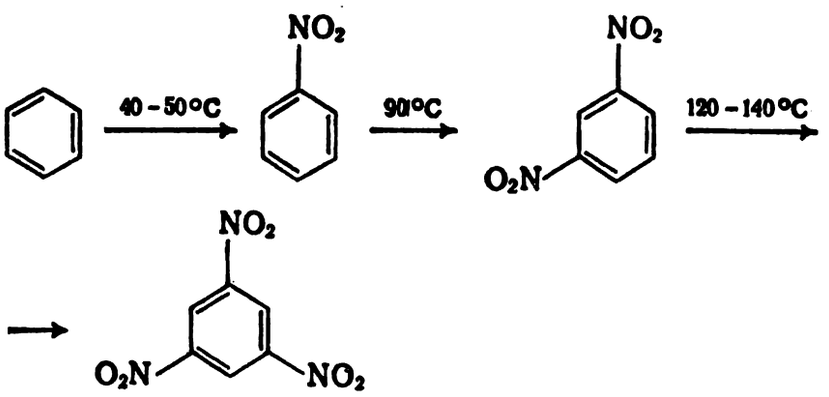
Other authors are of the opinion that other radical particles participate in the nitration of paraffins and cycloparaffins. An important fact is that the nitration reaction is not of a chain nature: active particles must be continuously created anew.

The nitration process is always accompanied by the partial degradation of the organic substance taken: by oxidation or the rupture of carbon-carbon bonds. For example, when propane is being nitrated, only 40 per cent of it is transformed into nitro compounds. The mixture of nitro compounds formed has the following composition:

$$CH_3—CH_2—CH_3 \xrightarrow[420°C]{HNO_3;} \underset{(9\%)}{CH_3NO_2} + \underset{(26\%)}{C_2H_5NO_2} + \underset{\substack{\text{1-Nitropropane (32\%);}\\ \text{2-Nitropropane (33\%)}}}{C_3H_7NO_2}$$

The replacement of hydrogen in the *aromatic nucleus* by the nitro group occurs according to a quite different mechanism. It is an electrophilic substitution reaction, and its mechanism has already been considered in detail on page 126. In this case, nitration is effected by a nitrating mixture at room or higher temperature.

Three nitro groups at the most can be directly introduced into the benzene nucleus, and every subsequent group is introduced under more rigid conditions. Being a *meta-directing* substituent, the nitro group reduces the ability of the aromatic nucleus to undergo electrophilic substitution reactions. This can be illustrated by taking the example of benzene nitration:



To obtain di- and trinitro compounds, use should be made of not only higher temperature, but also more highly concentrated nitric acid (fuming nitric acid), and oleum instead of sulphuric acid.

Not only different aromatic hydrocarbons (including polynuclear ones), but also compounds whose nucleus already has other groups, e.g., a halogen, a hydroxyl, a sulpho group and an amino group, can be subject to nitration. The compounds obtained are of great importance as intermediates for synthesizing dyes, pharmaceuticals, etc.

14.3. Physical and Chemical Properties. The physical properties of nitro compounds are closely connected with the specific features of the structure of the nitro group. The semipolar bond creates a considerably high dipole moment. This is clearly seen from a comparison of the dipole moments of different benzene derivatives of the $C_6H_5—X$ structure. The sharp growth of the dipole moment as nitroso compounds (ordinary double bond N=O) pass over to nitro compounds (semipolar bond $N^+—O^-$) is seen especially clearly:

	D		D
C_6H_5I	1.30	C_6H_5NO . . .	3.14
C_6H_5OH . . .	1.45	$C_6H_5NO_2$ . . .	4.01

The large dipole moment of nitro compounds confirms the electron structure ascribed to them.

Compounds with highly polar molecules differ from nonpolar ones by other physical properties as well. Charges of opposite signs of polar molecules are attracted, and such molecules are torn away

from one another with greater difficulty than nonpolar ones. Therefore, polar substances have elevated melting and boiling points. This becomes evident when the boiling points of nitroethane are compared with those of other ethane derivatives (in °C):

C_2H_5Br 38
C_2H_5OH 78
$C_2H_5NO_2$ 114

The physical properties of some nitro compounds are given in Table 14.1. Most nitro compounds are liquids which have rather

TABLE 14.1. **Physical Properties of Nitro Compounds**

Name	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}	Dipole moment, D	Water-solubility at 20°C, g/100 ml
Nitromethane	—28.6	101	1.138	3.17	9.5
Nitroethane	—89.5	114	1.051	3.19	4.5
Nitropropane	—104	131	1.001	3.57	1.4
Nitrobenzene	+5.8	211	1.223	4.01	0.2
α-Nitronaphthalene	57.8	304	—	3.98	Practically insoluble

high boiling points. Di- and polynitro compounds are solids. Nitro compounds are almost colourless when they are perfectly pure, but they usually contain impurities, which make them yellow. The density of the first representatives of the homologous series is higher than unity, and it diminishes as the hydrocarbon radical grows. Water-solubility decreases as the hydrocarbon radical increases, as is always observed in homologous series. Nitro compounds mix with organic solvents in all proportions and are themselves good solvents for many organic substances.

Chemical properties. *Reduction.* There is a certain similarity between nitro compounds and nitric acid in their chemical behaviour. This similarity is exhibited in oxidation-reduction reactions. The most characteristic property of nitric acid that distinguishes it from most other acids is its oxidizing action. This property is known well from the textbook of inorganic chemistry, where nitric acid is regarded as a strong oxidizing agent. In these reactions, nitric acid itself is reduced as it exhibits its oxidizing action. Nitro compounds are reduced themselves when they act, like nitric acid, as oxidizing agents. Different substances can be obtained from nitro compounds, depending on the reducing agents used and on the reaction conditions. Amines are the end and most important product:

$$R—NO_2+6H \longrightarrow R—NH_2+2H_2O$$

This reaction is quite similar to the electrochemical reduction of nitric acid to hydroxylamine:

$$HO—NO_2+6H \longrightarrow HO—NH_2+2H_2O$$

Electron-accepting Properties of the Nitro Group. Condensation Reactions. The nitro group is similar, by its strong positive charge on the nitrogen atom, to the carbonyl group with its positively charged carbon atom. Let us recall that the carbonyl group, while withdrawing electrons, increases the mobility of hydrogen atoms attached to the adjacent carbon atom, i.e., it increases their ability to be eliminated as a proton (see Sec. 11.4). The nitro group acts on α-hydrogen atoms in the same way.

The mobility of α-hydrogen atoms is exhibited in the ability of *primary* and *secondary* nitro compounds to act as a methylene component in condensation reactions with carbonyl compounds. These condensation reactions are of the aldol-croton type:

$$C_6H_5—C(=O)—H + CH_3NO_2 \longrightarrow \underset{\text{β-Nitro-α-phenylethyl alcohol}}{C_6H_5—CH(OH)—CH_2—NO_2} \xrightarrow[-H_2O]{} C_6H_5—CH=CH—NO_2$$

β-Nitrostyrene

Alkali Action. Nitro Compound Tautomerism. The mobility of the α-hydrogen atoms of primary and secondary nitro compounds is exhibited in their ability to react with alkalies. Let us consider this reaction by taking the example of phenylnitromethane, $C_6H_5CH_2NO_2$. This substance is a liquid which boils at 226°C and does not dissolve in water. But phenylnitromethane dissolves in aqueous alkaline solutions, forming a salt, in which the organic residue acts as an anion. When an acid carefully acts on this salt, phenylnitromethane is evolved as a solid of *aci*-form (m.p. 84°C). This form gradually turns into ordinary liquid phenylnitromethane:

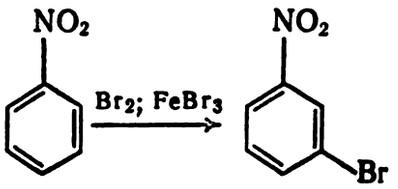
$$C_6H_5—CH_2—\underset{\downarrow}{\overset{\downarrow}{N}}=O \xrightarrow{NaOH} C_6H_5—CH=\underset{\downarrow}{N}—ONa \xrightarrow{HCl} C_6H_5—CH=\underset{\downarrow}{N}—OH$$

O O O

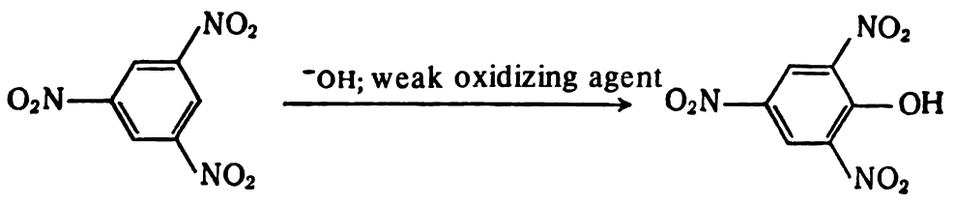
Besides nitro compounds, some other organic substances are capable of existing in several interconverting forms (*tautomerism*). Tautomerism is dealt with at greater length in Sec. 18.9.

Effect of the Nitro Group on the Aromatic Nucleus. The nitro group relates to meta-directing substituents: withdrawing electrons from the aromatic nucleus, it reduces its activity in electrophilic substi-

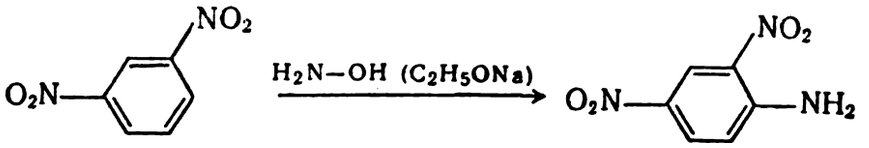
tution reactions. The entering substituent is directed into the *meta*-position:



Electron density diminishes especially greatly in the *ortho*- and *para*-positions towards a nitro group. *Ortho*- and *para*-positions of the nucleus that are depleted of their electrons become partially positively charged and at the same time become capable of undergoing *nucleophilic substitution* reactions, which are unusual for aromatic compounds, e.g.,

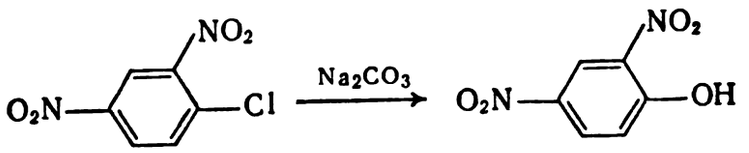


1,3,5-Trinitrobenzene — Picric acid



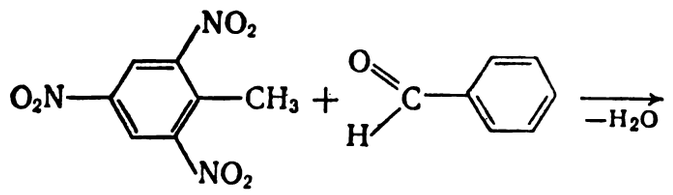
1,3-Dinitrobenzene — 2,4-Dinitroaniline

A halogen in *ortho-para*-positions becomes more reactive under the action of nitro groups:

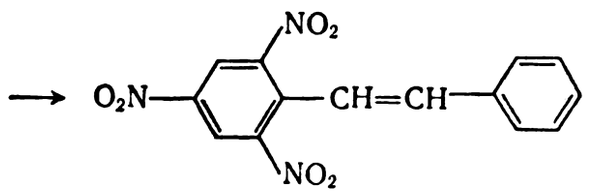


The effect of nitro groups extends also to the hydrogen atoms of the methyl group, which is linked with the benzene nucleus, i.e., it becomes capable of acting as a methylene component in condensa-

tion reactions with carbonyl compounds in the presence of bases:

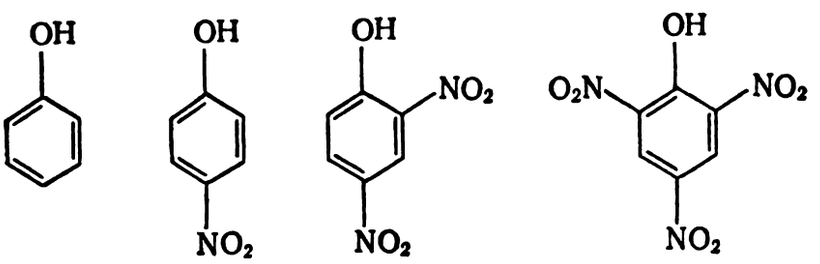


2,4,6-Trinitrotoluene



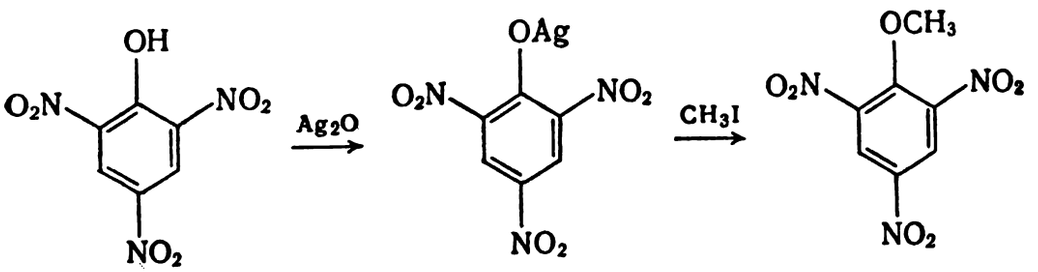
2,4,6-Trinitrostilbene

Withdrawing electrons from the nucleus, the nitro group also increases the acidity of the hydroxyl groups in *ortho-* and *para-* positions. The concerted action of several nitro groups produces an especially strong effect. The effect of nitro groups on the acidity of the phenol hydroxyl is clearly seen from the values of the acid dissociation constants K_a of the following compounds:



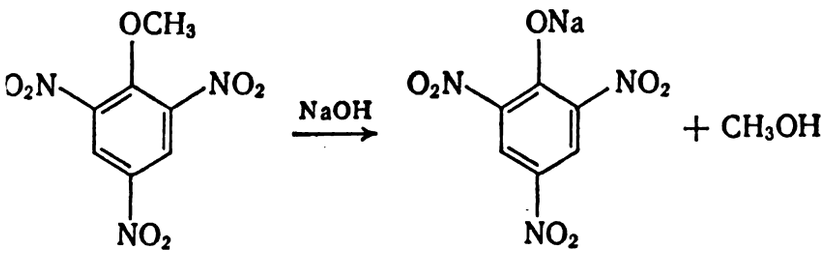
1.7×10^{-10} 0.96×10^{-7} 1×10^{-4} 4.2×10^{-1}

The last compound given in this series, 2,4,6-trinitrophenol, is called *picric acid.* Indeed, this substance acts as a real acid (it is stronger than carbonic acid), forming salts known as *picrates*:

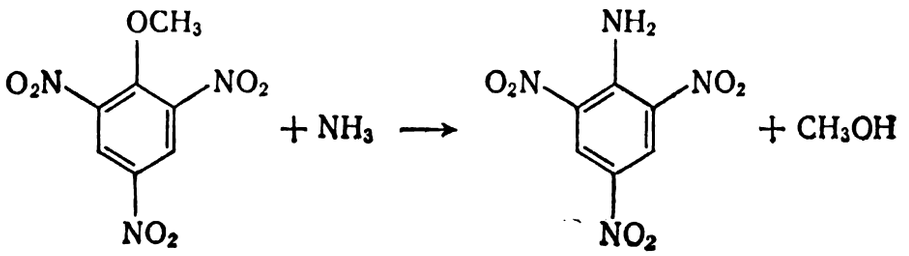


Picric acid Silver picrate Methyl picrate

Methyl picrate has ester properties; for example, it saponifies when boiled with alkalies:



This ester forms, with ammonia, the amide called *picramide*:



14.4. Important Nitro Compounds. Aliphatic nitro compounds. The first representatives of the homologous series with the number of carbon atoms in the C_1-C_3 range are produced industrially. These nitro compounds are used as solvents (particularly for synthetic resins and rubbers), and are also employed for various syntheses, i.e., for obtaining nitroalcohols, nitroolefins and other compounds. The production of hydroxylamine from nitroethane under the action of sulphuric acid is important industrially:

$$CH_3—CH_2—NO_2 \xrightarrow{H_2O(H^+)} CH_3—COOH + NH_2—OH$$

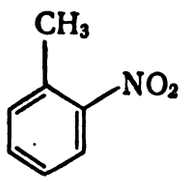
Acetic acid is obtained simultaneously.

All the nitro compounds are rather strongly poisonous for the central nervous system. Some of them act as an irritant. This applies, for example, to trichloronitromethane, CCl_3NO_2, which is used as an insecticide called *chloropicrin*. Chloropicrin is also a strong lachrymator, and it was used as a poisonous substance in warfare during World War I.

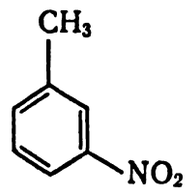
Nitrocyclohexane is a liquid which boils at 205°C. It is obtained industrially by nitrating cyclohexane by nitric acid in a liquid phase at 150°C and under elevated pressure. Nitrocyclohexane is transformed into cyclohexanone oxime, which is raw material for obtaining caprolactam, an initial substance in capron synthesis.

Nitrobenzene is a colourless liquid (it is usually yellow due to impurities) whose b.p. is 211°C, and d_4^{20}, 1.203. It is produced industrially in large amounts and is used mainly in reduction to aniline, $C_6H_5NH_2$.

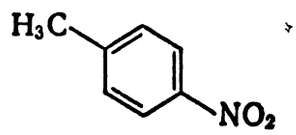
Nitrotoluenes exist as three isomers, and the most important of them are *ortho-* and *para*-isomers, which are formed when toluene is being nitrated. These isomers can be separated by freezing out the *para*-isomer.



o-Nitrotoluene
(m.p.–3°C)
(b.p. 222°C)



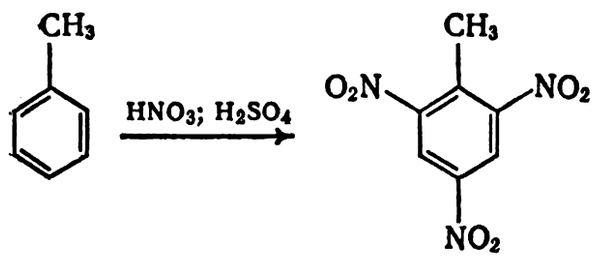
m-Nitrotoluene
(m.p. 16°C)
(b.p. 233°C)



p-Nitrotoluene
(m.p. 52°C)
(b.p. 238°C)

Nitrotoluenes are reduced to the corresponding amines, which are then used in dyestuff synthesis.

Trinitrotoluene (trotyl, TNT, tolite) is a product of exhaustive toluene nitration:



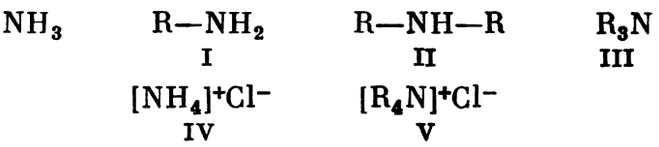
It is a solid (m.p. 80°C) and is one of the most widely distributed explosives. A valuable property of tolite is its rather low sensitivity to shock and friction, and therefore it is relatively safe. When it is ignited in the air, it burns smoothly, and an explosion may occur only when large amounts of it burn up or detonators are used.

α-Nitronaphthalene is a solid which melts at 61°C. It is obtained readily in naphthalene nitration. Its reduction gives α-naphthylamine, which is an initial substance for synthesizing other α-substituted naphthalenes.

Chapter 15

AMINES

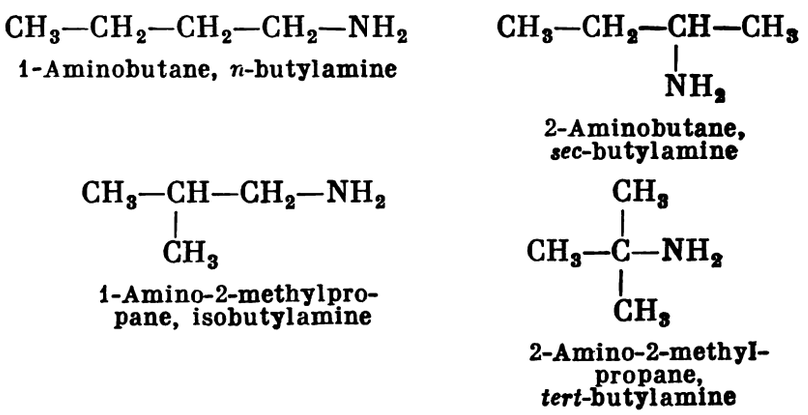
15.1. Structure. Isomerism. Nomenclature. Physical Properties. *Amines* are organic derivatives of ammonia that can be regarded as the products of replacement of hydrogen atoms of ammonia by hydrocarbon radicals. Amines can be aliphatic (saturated and unsaturated), alicyclic, aromatic and heterocyclic, depending on the nature of a radical. There are *primary* I, *secondary* II and *tertiary* III amines, depending on the number of hydrogen atoms replaced by radicals; organic derivatives of ammonium salts IV are *quaternary ammonium compounds* V:



The existence of amines of a different degree of substitution creates additional opportunities for isomerism and increases the number of possible compounds. Let us recall that the butane hydrocarbon has two isomers, alcohols derived from it have four isomers, while there are eight amines with the formula $C_4H_{11}N$.

The names of primary amines are composed from those of hydrocarbons by adding the prefix **amino** or the suffix **amine** to them. The names of secondary and tertiary amines are formed in most cases according to the principles of rational nomenclature, enumerating the radicals in a compound. This can be exemplified by the names of the above-mentioned isomeric amines $C_4H_{11}N$.

Primary amines:



Secondary amines:

$CH_3—CH_2—CH_2—NH—CH_3$

1-Methylaminopropane, methylpropylamine

$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—NH—CH_3$$

2-Methylaminopropane, methylisopropylamine

$CH_3—CH_2—NH—CH_2—CH_3$

Ethylaminoethane, diethylamine

Tertiary amine:

$$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{N}}—CH_3$$

Dimethylaminoethane, dimethylethylamine

The simplest aliphatic amines (methylamine, dimethylamine, trimethylamine and ethylamine) are gaseous substances, amines having a larger number of carbon atoms are liquids, and those beginning from $C_{12}H_{25}NH_2$ are solids. The odour of lower molecular weight amines is similar to that of ammonia. The first representatives of the series dissolve well in water, but water-solubility diminishes as the carbon skeleton grows. The physical properties of some amines are given in Table 15.1.

TABLE 15.1. **Physical Properties of Some Amines**

Name	Formula	Melting point, °C	Boiling point, °C	Relative density, d_4^{20}
Methylamine	CH_3NH_2	—	−7.6	0.769 (at −79°C)
Dimethylamine	$(CH_3)_2NH$	—	+7	0.680 (at 0°C)
Trimethylamine	$(CH_3)_3N$	−117	3.5	0.671 (at 0°C)
Ethylamine	$C_2H_5NH_2$	—	16.6	0.706 (at 0°C)
Diethylamine	$(C_2H_5)_2NH$	−50	56	0.711
Propylamine	$C_3H_7NH_2$	—	49	0.714
Butylamine	$C_4H_9NH_2$	—	78	0.742
Hexylamine	$C_6H_{13}NH_2$	−19	130	0.763
Aniline	$C_6H_5NH_2$	−6	184	1.027
Methylaniline	$C_6H_5NHCH_3$	—	196	0.989
Dimethylaniline	$C_6H_5N(CH_3)_2$	2.5	194	0.956
Diphenylamine	$(C_6H_5)_2NH$	54	302	1.158

15.2. Preparation of Amines. The methods of obtaining amines are very diverse, but the main ones are ammonia alkylation (*Hofmann reaction*) and the reduction of nitro compounds. The first reaction is used mainly for obtaining amines of the aliphatic series, and the second one is the main way of synthesizing aromatic amines.

1. Alkylation of ammonia. In this case, hydrocarbon radicals gradually replace the hydrogen atoms of ammonia with the formation of a mixture of amines of all the degrees of substitution (as salts), e.g.,

$$NH_3 + C_2H_5Br \longrightarrow C_2H_5\overset{+}{N}H_3\ Br^- \xrightarrow{NH_3} C_2H_5NH_2 + NH_4Br$$

$$C_2H_5NH_2 \xrightarrow{C_2H_5Br} (C_2H_5)_2\overset{+}{N}H_2\ Br^- \xrightarrow{NH_3} (C_2H_5)_2NH + NH_4Br$$

$$(C_2H_5)_2NH \xrightarrow{C_2H_5Br} (C_2H_5)_3\overset{+}{N}H\ Br^- \xrightarrow{NH_3} (C_2H_5)_3N + NH_4Br$$

$$(C_2H_5)_3N \xrightarrow{C_2H_5Br} (C_2H_5)_4\overset{+}{N}\ Br^-$$

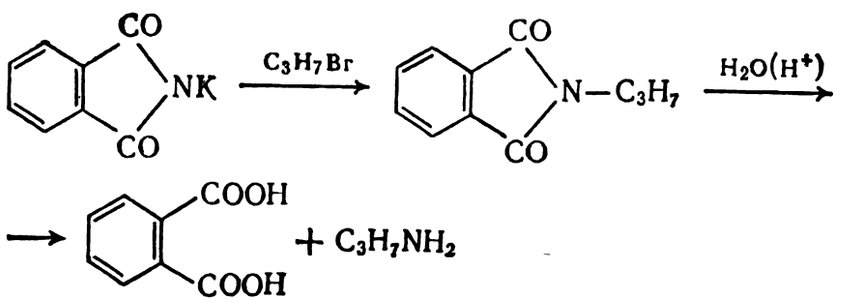
This reaction is a classical example of nucleophilic substitution: a positive charge originates on the carbon atom as a result of the polarization of the C—Br bond, the primary attack of the ammonia being at the pair of unshared electrons on nitrogen.

A mixture of salts of primary, secondary and tertiary amines and quaternary ammonium bases is formed when ammonia is being alkylated by the Hofmann reaction. Therefore, this reaction is not very convenient for obtaining primary amines. It is used more often for obtaining *secondary* and *tertiary* amines, e.g., monomethylaniline and dimethylaniline from aniline. Instead of alkyl halides, methyl alcohol is used as a cheaper alkylating agent for industrially carrying out this reaction. The reaction occurs on heating under pressure:

$$C_6H_5NH_2 + CH_3OH \longrightarrow C_6H_5NHCH_3 + H_2O$$

$$C_6H_5NHCH_3 + CH_3OH \longrightarrow C_6H_5N(CH_3)_2 + H_2O$$

Alkylation of not ammonia proper, but some of its derivatives, is effected in order to obtain *primary* amines. In one variant, for instance, potassium phthalimide (*Gabriel synthesis*) is used as starting material:



2. Reduction of aromatic nitro compounds. This reaction was first effected by N. N. Zinin (1842). He obtained aniline by treating nitrobenzene with ammonium sulphide:

$$C_6H_5NO_2 + 3(NH_4)_2S \longrightarrow C_6H_5NH_2 + 6NH_3 + 3S + 2H_2O$$

Zinin's discovery initiated the development of the aniline-dye industry. A well-known statement made by A. Hofmann is that Zinin's name deserves to be written in gold letters in the history of chemistry for this discovery alone.

Other reducing agents, such as tin, zinc, iron in an acid medium, stannous chloride, and hydrogen over catalysts, can also be used for transforming nitro compounds into amines. Reduction can be effected electrochemically as well.

The reduction of nitrobenzene to aniline under the action of iron in the presence of hydrochloric acid is now of the greatest importance in technological processes. There is no need to take large amounts of hydrochloric acid when the process is being effected industrially. After traces of $FeCl_2$ are formed, reduction occurs further at the expense of water and metallic iron according to the summary equation:

$$4C_6H_5NO_2 + 9Fe + 4H_2O \longrightarrow 4C_6H_5NH_2 + 3Fe_3O_4$$

In the laboratory, nitro compounds are reduced to amines often by tin and hydrochloric acid:

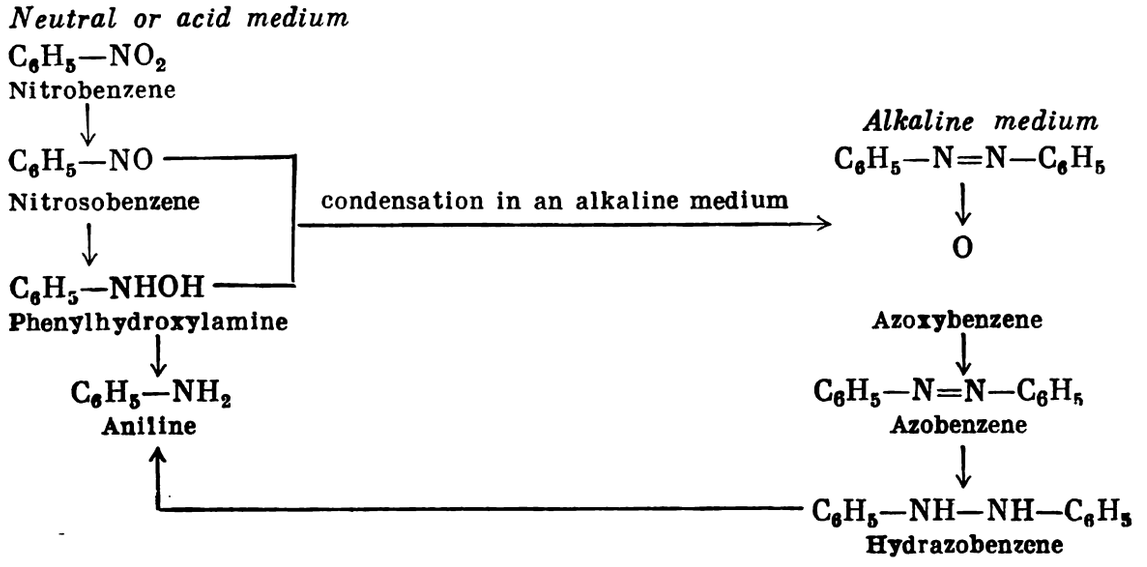
$$C_6H_5NO_2 + 3Sn + 7HCl \longrightarrow C_6H_5NH_2 \cdot HCl + 3SnCl_2 + 2H_2O$$

A convenient modern laboratory method of reducing nitro compounds is based on the use of hydrazine in the presence of Raney nickel as a catalyst:

$$2C_6H_5NO_2 + 3H_2N{-}NH_2 \xrightarrow{Ni} 2C_6H_5NH_2 + 4H_2O + 3N_2$$

This method is advantageous, because the reaction products do not contain any substances which hinder the isolation of amine by the simple distillation of the reaction mixture.

Nitro compounds are reduced to amines through several intermediate stages. The structure of intermediate products depends on the type of a reducing agent and on the reaction conditions (especially on the acidity of the medium). The diversity of intermediate reduction products is illustrated by the following scheme:

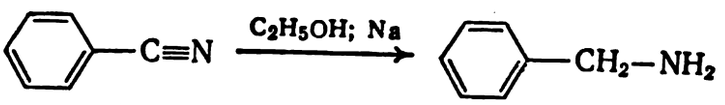


All the intermediate products become amines as reduction is effected further.

3. Other nitrogen-containing compounds, such as oximes, nitriles and amides, can also be reduced to amines:

$$(CH_3)_2C{=}N{-}OH \xrightarrow{C_2H_5OH;\ Na} (CH_3)_2CH{-}NH_2$$

Acetoxime — Isopropylamine



Benzonitrile — Benzylamine

$$CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \xrightarrow{LiAlH_4} CH_3{-}CH_2{-}CH_2{-}NH_2$$

Propionamide — Propylamine

4. A peculiar method of obtaining amines is the *Hofmann rearrangement.* In this reaction, amide is transformed into amine with a loss of one carbon atom, which is eliminated as CO_2. The amino group, which is initially attached to carbonyl carbon, shifts towards the hydrocarbon radical, i.e., *intramolecular rearrangement* occurs:

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + NaOBr + 2NaOH \longrightarrow CH_3{-}NH_2 + Na_2CO_3 + NaBr + H_2O$$

15.3. Basicity of Amines. Amines, being organic derivatives of ammonia, retain its main chemical features. In particular, amines, like ammonia, exhibit basic properties. This is revealed by the alkaline reaction of aqueous amine solutions:

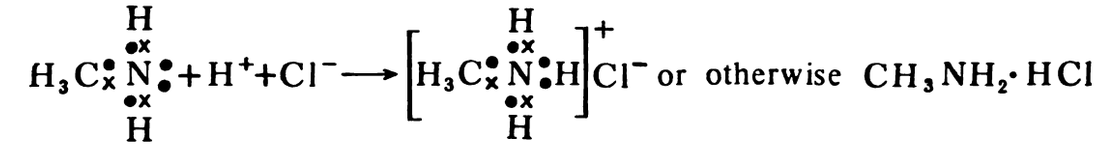
$$NH_3 + H_2O \rightleftarrows NH_4^+ + HO^-$$

$$RNH_2 + H_2O \rightleftarrows RNH_3^+ + HO^-$$

The water-solubility of amines decreases as the hydrocarbon residue increases. Therefore, higher amines no longer produce an alkaline reaction. But they also retain basic properties, and this is revealed by their ability to form salts with acids. Their basic properties are due to the pair of *unshared electrons on nitrogen.*

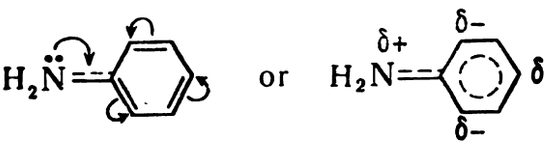
In ammonia or amines, the nitrogen atom spends only three electrons out of its five valence electrons on the formation of covalent bonds. Two electrons remain free, and a proton may be added at the expense of this free electron pair, causing the formation of

ammonium salts:



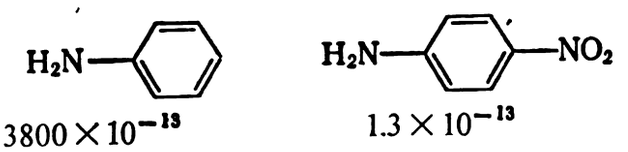
In quaternary ammonium compounds, nitrogen forms four perfectly the same covalent bonds, and it is tetracovalent; the fifth valence is an ionic one: the positively charged ammonium grouping retains the anion by ordinary electrostatic attraction.

The nature of the radical, with which an amino group is linked, affects the basic properties of amines. In particular, aromatic amines are much weaker bases than amines of the aliphatic series, because the free electron pair of amine nitrogen becomes conjugated with the mobile electrons of the aromatic ring. The distribution of electron density in aniline can be expressed by the following formula:



Such a distribution reduces electron density on the nitrogen atom and, consequently, makes it less capable of adding a proton.

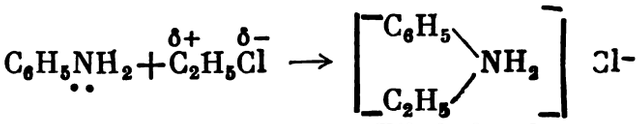
The basicity of the amino group decreases further when a nitro group possessing electron-accepting properties is introduced into the aniline nucleus. This follows from a comparison of the basicity constants K_b of aniline and *p*-nitroaniline:



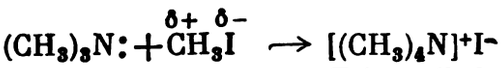
3800×10^{-13} 1.3×10^{-13}

15.4. Chemical Properties. The free electron pair of the nitrogen atom determines not only the basicity of amines, but also many other of their properties. Amine reactions begin in most cases by an interaction between the free electron pair and electrophilic reagents, i.e., substances whose reaction centre is positively charged (lack of electrons). Some reactions end with this, while others are followed by the stage of elimination after addition. The most important amine reactions are:

Alkyl halide addition. Ammonium salts formed in the reaction are stable, and the reaction ends with their formation:

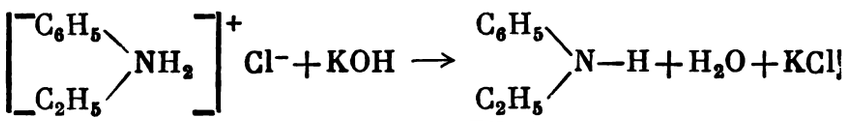


Ethyl phenyl ammonium chloride

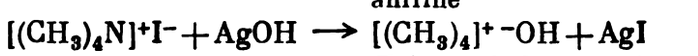


Tetramethyl ammonium iodide

The corresponding amines and tetra-substituted ammonium bases can be isolated in a free state by subjecting the salts formed to the action of bases:



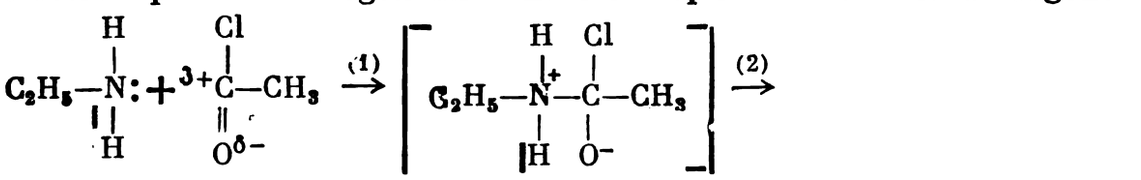
Ethyl-aniline



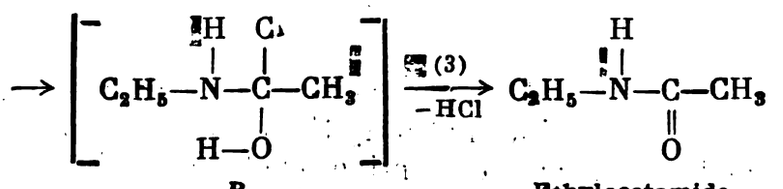
Tetramethyl ammonium hydroxide

When both reactions are consecutively carried out, secondary amine is obtained from the primary one, and tertiary amine, from the secondary one, while the quaternary ammonium base is obtained from tertiary amine. As a result, a new hydrocarbon radical instead of hydrogen is added to the nitrogen atom, i.e., *amine is alkylated.*

Acylation reaction. Acyl amides are formed when amines react with acyl chlorides, anhydrides or esters. The process begins like alkylation, i.e., it begins with the interaction between the free electron pair of nitrogen and the electrophilic centre of a reagent:



A



B

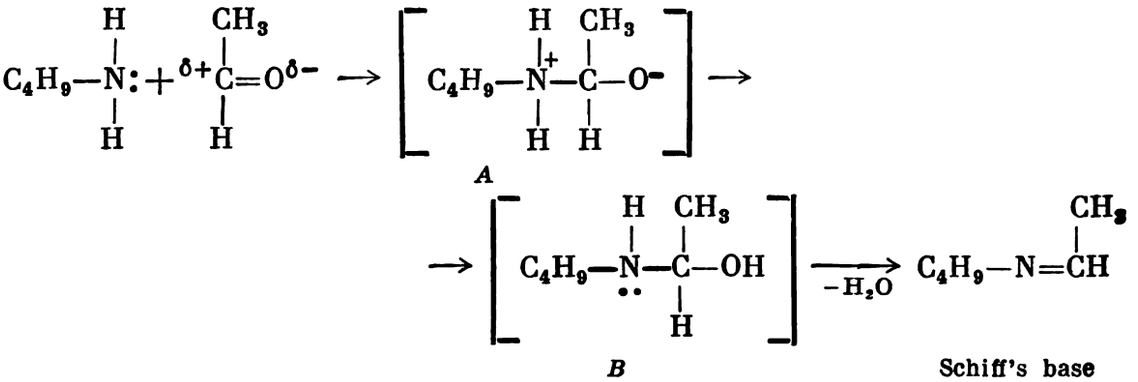
Ethylacetamide

The addition product is formed owing to the interaction between the free electron pair of nitrogen and carbonyl carbon, which bears a partial positive charge as a result of the polarization of the C=O bond. In this case, nitrogen shares the electron pair with carbonyl

carbon. But the latter already had its octet on the outer electron shell filled up prior to the reaction, and it cannot accept another electron pair. Therefore, as a bond is established between nitrogen and carbonyl carbon, the mobile electron pair of the C=O π-bond is driven back to the oxygen atom, which thus becomes negatively charged (stage 1). In the structure formed (intermediate product *A*), the positively charged centre (nitrogen) and the negatively charged one (oxygen) are close to one another. The natural tendency towards neutralization is effected as a proton passes over from nitrogen to oxygen, which possesses, in addition, greater electronegativity (stage 2). But compounds like the intermediate product *B* that have a hydroxyl group and a halogen at one carbon atom are unstable. Stabilization is caused by the elimination of hydrogen chloride (stage 3). The final result of the reaction is the entering of the acyl group (CH_3CO—) instead of the hydrogen atom to nitrogen, i.e., *amine acylation.*

Reactions with aldehydes and ketones. These reactions also occur through intermediate addition products (as formerly, they are denoted by *A* and *B*). Stabilization is effected in different ways for primary and secondary amines (tertiary amines do not react).

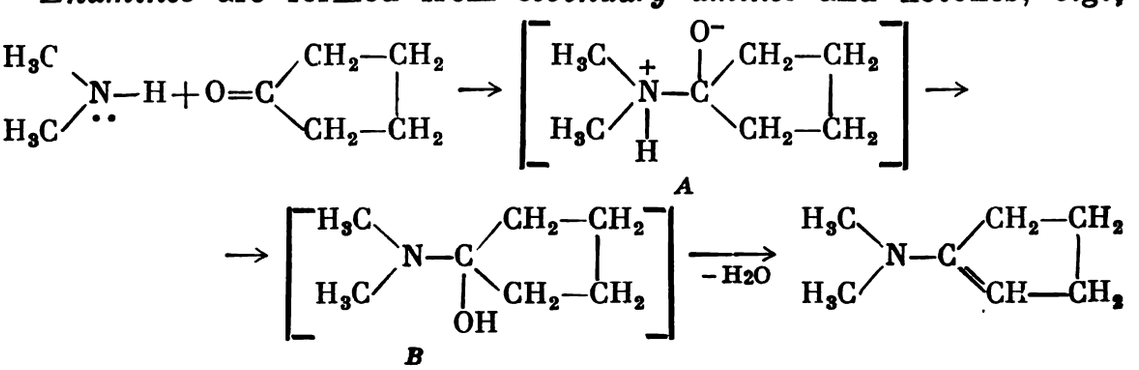
Schiff's bases, or *imines*, are formed from *primary amines* and aldehydes (ketones enter into this reaction with greater difficulty) as water is eliminated:



A *B* Schiff's base

Similar compounds formed in the reaction between aniline and aldehydes are called *anils.*

Enamines are formed from *secondary amines* and ketones, e.g.,



A *B*

In this case, the addition product contains only one hydrogen atom attached to nitrogen: this atom passes over to oxygen when the intermediate product *A* is being stabilized, while mobile hydrogen, which is at the α-carbon atom, participates in water formation.

Reactions with nitrous acid. A nitrite and a strong mineral acid are taken practically for carrying out these reactions. It is supposed that, in this case, the *nitrosonium ion*, $\overset{+}{N}{=}O$, is formed: this ion is a relatively weak electrophilic particle (like the *nitronium ion*, $\overset{+}{N}O_2$, in nitration reactions):

$$NaNO_2 + HCl \longrightarrow H{-}O{-}N{=}O + NaCl$$

$$H{-}O{-}N{=}O + HCl \longrightarrow H_2O + \overset{+}{N}{=}O + Cl^-$$

Like the reactions considered earlier, the free electron pair of amine nitrogen at first reacts with the nitrosonium ion. The intermediate addition products obtained are stabilized in different ways, and therefore the end products are different, notwithstanding the fact that reactions with primary, secondary, tertiary, aliphatic and aromatic amines have a common mechanism.

Primary aliphatic amines are subjected to deamination with the evolution of nitrogen and the formation of *alcohols* or *unsaturated hydrocarbons*. The reaction occurs through the intermediately formed diazo compound (propyl diazonium chloride in the example), from which nitrogen is eliminated with the formation of the carbonium ion. This carbonium ion is stabilized in different ways: it becomes alcohol as it adds the hydroxyl anion (from water), or an unsaturated hydrocarbon as it loses a proton, e.g.,

$$CH_3CH_2CH_2{-}\overset{H}{\underset{H}{N}}{:} + \overset{+}{N}{=}O \xrightarrow{Cl^-} \left[CH_3CH_2CH_2{-}\overset{H}{N}{-}N{=}O \right]^+ Cl^- \xrightarrow[-H_2O]{}$$

$$\longrightarrow [CH_3CH_2CH_2{-}N{\equiv}N]^+ Cl^- \xrightarrow[-N_2]{}$$

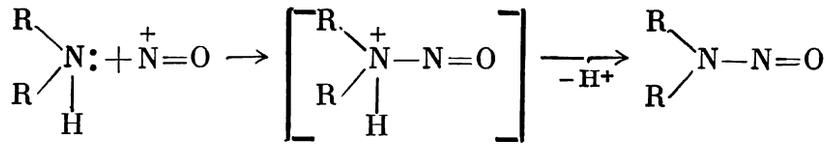
Propyl diazonium chloride

$$\longrightarrow [CH_3CH_2CH_2]^+ \begin{cases} \xrightarrow{+HO^-} CH_3{-}CH_2{-}CH_2OH \\ \xrightarrow[-H^+]{} CH_3{-}CH{=}CH_2 \end{cases}$$

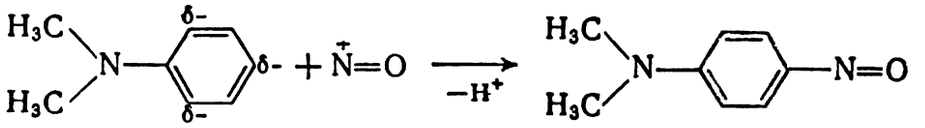
n-Propyl cation

The reaction between nitrous acid and primary aromatic amines is especially important; in this reaction, it is possible to stop at the stage of *diazo compounds* (see Chap. 16).

Secondary amines (aliphatic and aromatic ones) yield N-*nitrosamines* under the action of nitrous acid:



Tertiary amines of the aliphatic series form, with nitrous acid, only unstable salts, while those of the aromatic series form *p*-nitroso compounds, e.g.,

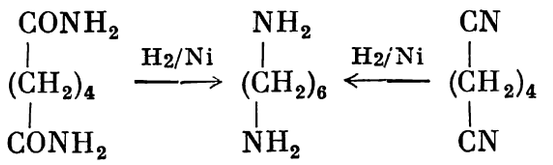


Dimethylaniline *p*-Nitrosodimethylaniline

This reaction occurs as ordinary electrophilic substitution in the aromatic nucleus, greatly activated by the tertiary amino group.

15.5. Important Individual Amines. The simplest aliphatic amines, i.e., *methylamine*, *dimethylamine* and *diethylamine*, are used for synthesizing medicinals, vulcanization accelerators and other products of organic synthesis.

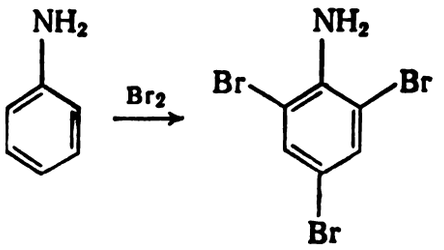
Hexamethylenediamine, $H_2N—(CH_2)_6—NH_2$, is one of the initial substances for obtaining the important polymeric material Nylon, (see Sec. 23.7). Therefore, hexamethylenediamine is produced industrially in large amounts by hydrogenating an amide or nitrile of adipic acid:



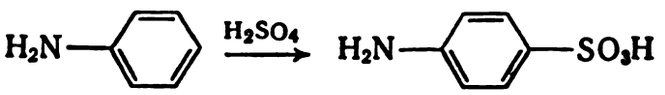
Aniline, $C_6H_5NH_2$, is the most important aromatic amine. It is produced industrially in large amounts by reducing nitrobenzene with iron filings in the presence of water and small amounts of hydrochloric acid. The catalytic reduction of nitrobenzene by hydrogen in a gaseous phase is now also of great industrial importance. Chlorobenzene can be converted into aniline by passing its mixture with ammonia at 400°C over cuprous salt as a catalyst. Aniline is used for obtaining dyes, medicinals, vulcanizates and stabilizers for rubber, plastics and photographic developers.

The basic properties of aniline are weakened by the effect of the aromatic nucleus on the amino group (the basicity constant of aniline is 3.8×10^{-10}, while that of methylamine is 5×10^{-4}). In turn, the amino group affects the aromatic nucleus: being an

electron-donating substituent, it increases electron density in the nucleus, thus facilitating electrophilic substitution reactions. Aniline is readily brominated, forming tribromoaniline already under the action of bromine water:

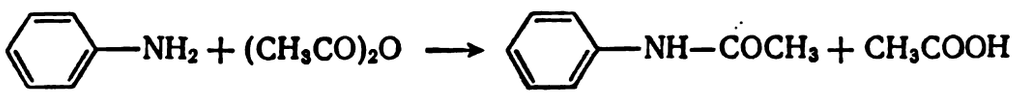


When aniline is heated with concentrated sulphuric acid, it sulphonates with the formation of *sulphanilic acid*, which is an important intermediate product in the synthesis of dyes and medicinals:

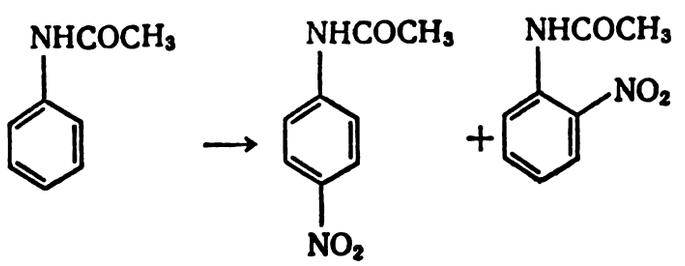


Aniline is readily oxidized. Therefore, it usually darkens on storage, although it is colourless when perfectly pure. An intense violet colour appears as a result of oxidation when bleaching powder acts on an aqueous solution of aniline (whose water-solubility is 3.6 per cent). This colour reaction is a qualitative test for aniline.

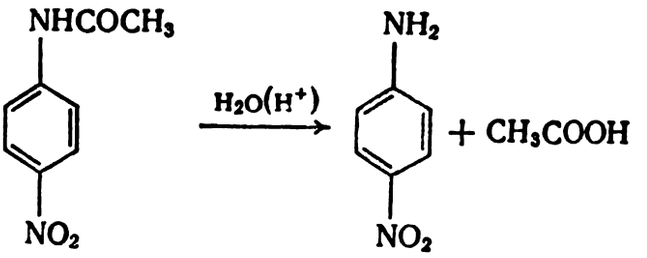
Nitric acid also acts as an oxidizing agent on aniline. Therefore, the amino group is *protected* prior to nitration, transforming aniline into *acetanilide*:



Acetanilide is nitrated, forming mainly *p-nitroacetanilide* and a small amount of the *ortho*-isomer:



Nitroacetanilides are hydrolyzed to *nitroanilines* when they are heated together with dilute acids:

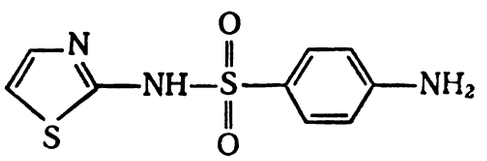


Nitroanilines are yellow solids used as a dye intermediate.

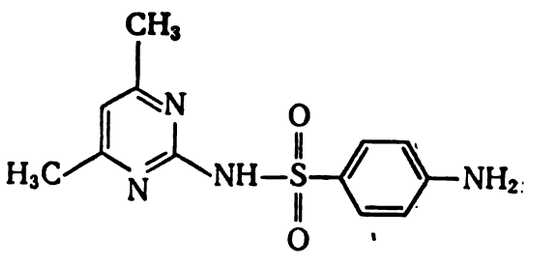
Diagram 15.1 (p. 330) gives an idea about the diversity of the products obtained industrially from aniline.

Sulphanilic acid, $HO_3S—C_6H_4—NH_2$, is a solid which precipitates as lustrous scales from hot water on crystallization, and it melts at approximately 290°C (decomposition). As we have already seen, it is obtained in aniline sulphonation. Sulphanilic acid possesses basic properties owing to the amino group, and acidic properties owing to the sulpho group; it is an *internal salt*, and this can be represented by the following formula: $H_3N^+—C_6H_4—SO_3^-$.

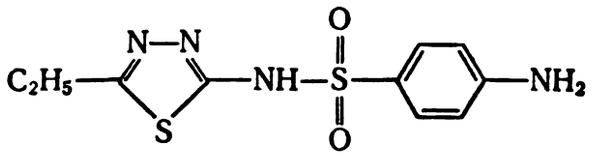
The most important derivative of sulphanilic acid is its amide (sulphanilamide), $H_2N—C_6H_4—SO_2—NH_2$. This colourless crystalline substance, which dissolves sparingly in cold water and well in hot water, is the base of an important class of medicinals: *sulpha drugs*. The simplest of them is sulphanilamide proper, or *Streptocid*. There are also many of its derivatives, i.e., products of substitution of various organic residues for the hydrogen atom of the amide group:



Sulphathiazole



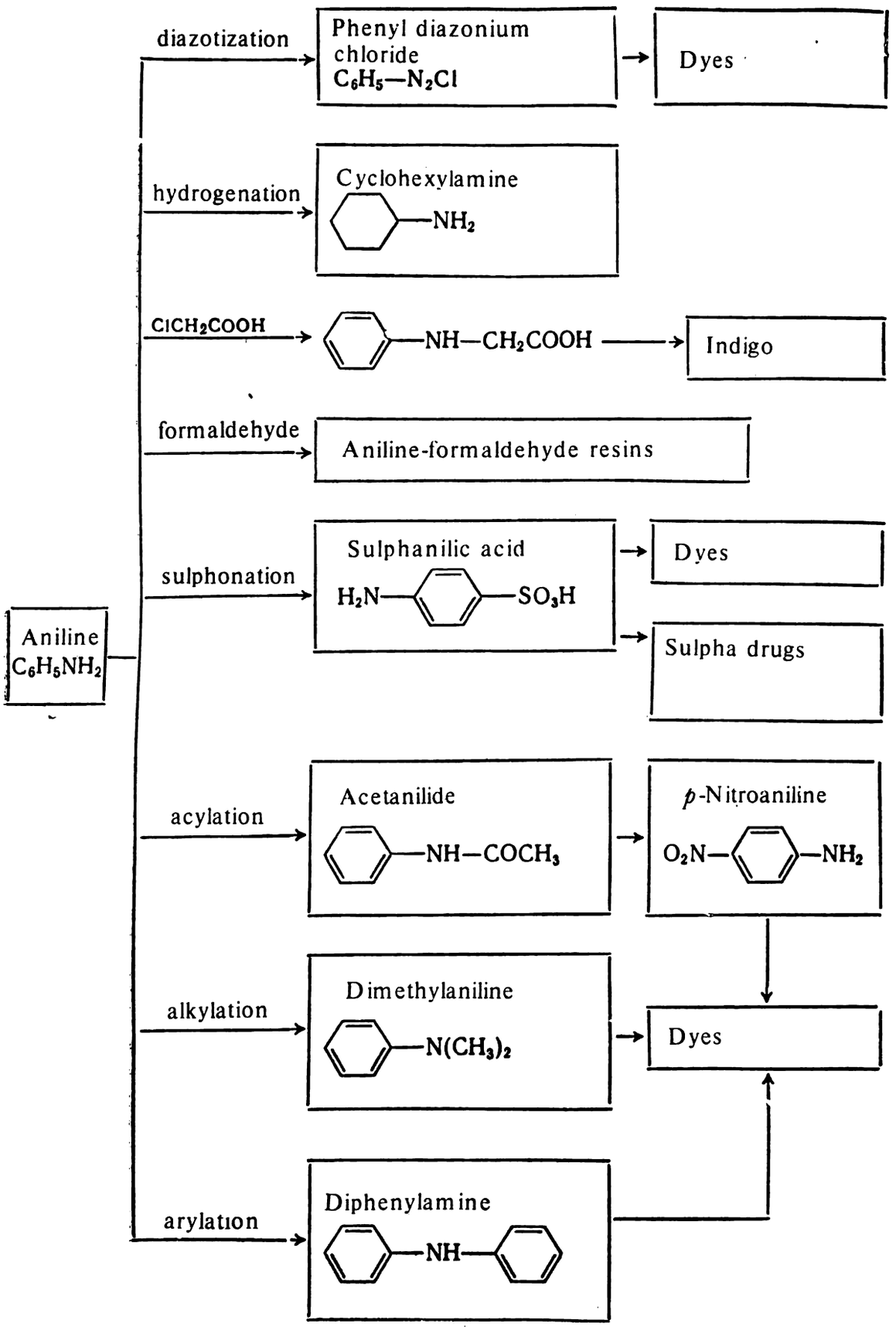
Sulphadimethazine



Sulphaethidole

The medicinal effect of sulpha drugs was discovered in the early 1930's. Since then, over six thousand compounds of this group have been synthesized, but only about 20 compounds are used in practice. At present, sulpha drugs are widely employed in the medical treat-

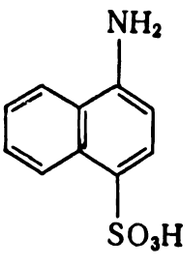
DIAGRAM 15.1. **Aniline-Based Products**



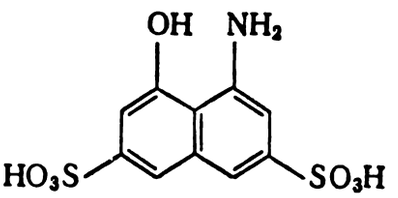
ment of various infectious diseases: angina, meningitis, erysipelas, dysentery, and many others. But it should be borne in mind that the uncontrolled use of sulpha drugs can be detrimental to health; in particular, it may seriously affect the kidneys.

Naphthylamines, $C_{10}H_7NH_2$, exist, like other monosubstituted naphthalenes, as two isomers (α- and β-naphthylamines). These compounds, especially their sulpho or hydroxy derivatives, are of great importance as dye intermediates.

Most of them have trivial names, e.g.,



Naphthionic acid (1-aminonaphthalene-4-sulphonic acid)



H acid (1-amino-8-hydroxy-naphthalene-3,6-disulphonic acid)

It has been discovered that β-naphthylamine is carcinogenic (it causes cancer of the urinary bladder), and therefore it is not used industrially in the Soviet Union.

Diphenylamine consists of colourless crystals which are practically insoluble in cold water. It is obtained when a mixture of aniline and aniline hydrochloride is heated under pressure:

$$C_6H_5NH_2 + C_6H_5NH_2 \cdot HCl \longrightarrow C_6H_5—NH—C_6H_5 + NH_4Cl$$

The basic properties of diphenylamine are even less pronounced than those of aniline. Diphenylamine forms salts only when it dissolves in concentrated acids. These salts are hydrolyzed when diluted with water, and a free base precipitated. Diphenylamine is used for obtaining dyes and in other syntheses. Blue colour appears when it is being oxidized; this reaction is employed for detecting nitric acid and other oxidizing agents.

Dimethylaniline, $C_6H_5N(CH_3)_2$, is a liquid which boils at 194°C; it is an important intermediate product in synthesizing dyes, explosives, and colour photographic developers. It is obtained from aniline by alkylation with methyl alcohol (p. 320).

15.6. Role of Electron Effects in Electrophilic Substitution in the Aromatic Nucleus. Now that we are acquainted with the structure and properties of the principal functional groups, we can continue our earlier (see Sec. 7.6) consideration of orientation in electrophilic substitution in the aromatic nucleus.

The substituents at the aromatic nucleus may either increase or decrease electron density in the nucleus. The nucleus can be affected

in two ways: by the inductive effect and by the mesomeric effect (conjugation effect).

The inductive effect causes the shift of electron density of single bonds (i.e., their polarization, see Sec. 9.7).

The inductive effect, being exhibited in the attraction of electrons by the substituent, is regarded as a *negative effect* and is denoted by $-I$; the effect which consists in the repulsion of electrons by the substituent is a *positive inductive effect* and is denoted by $+I$. The corresponding substituents are called also electron acceptors ($-I$ effect) and electron donors ($+I$ effect). By the strength and direction of the inductive effect, the substituents can be arranged in a series, where the hydrogen atom is used as an arbitrary standard for comparison:

$-I$ effect:

$$(CH_3)_3\overset{+}{N} > NO_2 > CN > CO > COOR > F > Cl > Br > I > OH > NH_2 > H$$

$+I$ effect:

$$H < CH_3 < C_2H_5 < \textit{iso}\text{-}C_3H_7 < \textit{n}\text{-}C_3H_7 < C(CH_3)_3$$

The *mesomeric effect* is exhibited in conjugated systems. It is a *negative* effect ($-M$) if the substituent *withdraws* electrons from the conjugated system, and a *positive* one ($+M$) when the substituent gives away its free electron pair for participation in common conjugation.

Substituents are arranged in the following series by the sign and strength of the mesomeric effect:

$$\underset{-M \text{ (electron acceptors)}}{NO_2 > CN > CO > COOH > H}$$

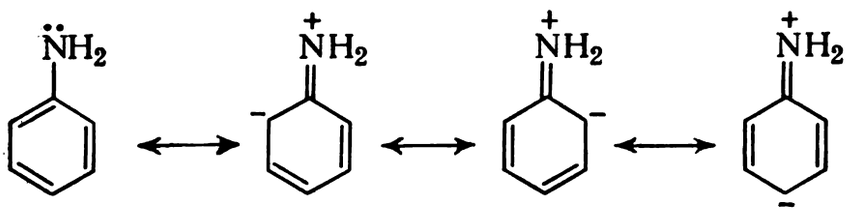
$$\underset{+M \text{ (electron donors)}}{H < Br < Cl < OCH_3 < OH < NH_2 < O^-}$$

A comparison of the foregoing series for mesomeric and inductive effects shows that the sign of both effects for a specific group can be either the same or different.

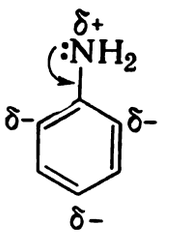
The nature of the orienting action of a substituent is determined by the sign of the inductive or mesomeric effect which it exhibits. Substituents for which the $+M$ or $+I$ effect predominates relate to *ortho-para*-orienting substituents, while substituents for which the $-M$ or $-I$ effect prevails are *meta*-orienting substituents.

Let us take the example of aniline to see how the electron effects in the aromatic nucleus are transferred mainly in the *ortho-* and *para*-positions. The amino group exhibits mainly the $+M$ effect. As a result, the electron density of the free electron pair of the nitrogen atom partially shifts towards the aromatic nucleus. A complete shift would mean the formation of the double bond N=C. In this

case, the carbon atom C_1 would have its octet filled up at the expense of the available four bonds, and cyclic conjugation in the aromatic nucleus would thus be disturbed. Six π-electrons would then have to be distributed in localized, fixed double bonds. But if valence rules are taken into account, only two double bonds can be formed in the ring, while one electron pair remains free. An ordinary formula of aniline and three structures, which are obtained after the given shift and which differ by the arrangement of the double bonds and the free electron pair*, are given below:



These formulas are *extreme structures* which are used to represent the mesomeric state of the aniline molecule. It can be represented also by one formula:



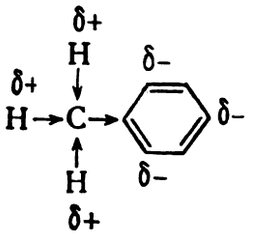
Both techniques of representing the distribution of electron density in the aniline molecule show that the negative charge is concentrated in *ortho-* and *para*-positions, i.e., it is there that favourable conditions are created for electrophilic substitution.

The hydroxyl group also has a positive mesomeric effect. The free electron pair of the oxygen atom of the OH group of phenol becomes conjugated with the aromatic nucleus, and heightened electron density is created in *ortho-para*-positions, like in aniline.

The *ortho-para*-orienting action of alkyl groups is of a different nature: their $+I$ effect is exhibited in this case. In the H—C bonds, a partial negative charge is borne by the carbon atom, i.e., a part of the electron density accumulated on it is transferred to the nucleus

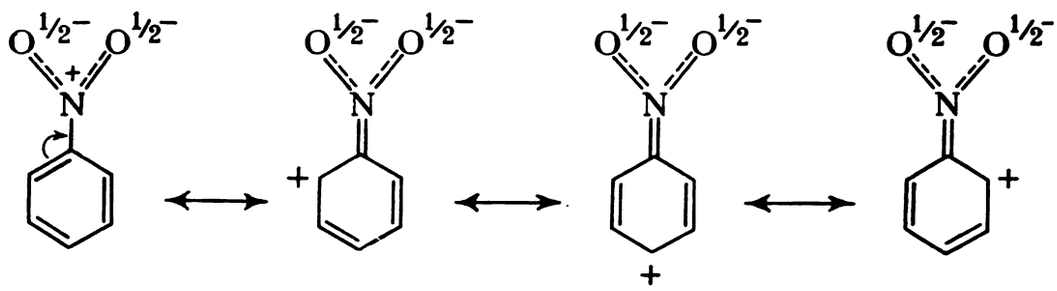
* The free electron pair cannot be put in the *meta*-position and, in this case, double bonds cannot be distributed in the ring.

and concentrated mainly in *ortho-para*-positions:



By increasing electron density in the nucleus, *o,p*-orienting substituents intensify the activity of the aromatic nucleus in electrophilic substitution reactions. An exception is only halogens, which, while being *ortho-para*-orienting substituents, reduce the reactivity of the aromatic nucleus. This is seen from a peculiar correlation between the nature of the inductive effect and that of the mesomeric effect of halogens. Halogens, which have a strong $-I$ effect, draw away electrons from the nucleus and reduce its electron density, thus lessening its reactivity. At the same time, the free electron pair of the halogen atom is partially transferred to the *ortho-* and *para*-positions of the aromatic nucleus due to the weak $+M$ effect inherent in halogens, and this makes halogens *o,p*-orienting substituents.

A typical *meta*-orienting substituent is the nitro group, which withdraws electrons from the nucleus at the expense of both $-M$ and $-I$ effects. In this case, the negative mesomeric effect causes electron density to be drawn out from the nucleus and a *positive* charge to appear in *ortho-* and *para*-positions:



The inductive effect of the nitro group acts in the same direction.

Another strong *meta*-orienting substituent, the ammonium group, causes, as a result of its positive charge, electron density to be withdrawn from the nucleus by the inductive mechanism.

Consequently, a *positive charge* in *ortho-* and *para*-positions appears under the action of *meta*-orienting substituents. In *meta*-positions, electron density does not decrease so strongly, and therefore the action of electrophilic reagents is directed to these sites. The nucleus is less reactive in electrophilic substitution, because its total electron density is reduced.

Electron effects and the orienting action of substituents are given in Table 15.2.

TABLE 15.2. **Orienting Action of Substituents**

Substituents	Electron effects	Substitution orientation	Effect on the nucleus
	Ortho-para orientants		
Alkyls	$+I$	*ortho-para-*	Activation
Amino group	$+M \gg -I$	*ortho-para-*	Ditto
Hydroxyl	$+M \gg -I$	*ortho-para-*	Ditto
Halogens	$+M < -I$	*ortho-para-*	Passivation
	Meta-orientants		
Nitro group	$-M, \ -I$	*meta-*	Passivation
Carboxyl group	$-M, \ -I$	*meta-*	Ditto
Ammonium group	$-I$	*meta-*	Ditto

Chapter 16

DIAZO COMPOUNDS

Diazo compounds, Ar—N_2X, are organic substances having a functional group which consists of two nitrogen atoms and is combined with an aromatic radical and an inorganic residue X. The structure of the N_2 group in diazo compounds will be deciphered somewhat later. A group of the same composition, which has the structure —N=N— and stands *between two* organic radicals (aromatic ones in most cases), begins another class known as *azo compounds*, R—N=N—R. They will be discussed also in this chapter.

16.1. Diazotization Reaction and the Structure of Diazo Compounds. A general and the most important method of obtaining diazo compounds is by the action of nitrous acid on the salts of primary aromatic amines (diazotization reaction). Instead of nitrous acid, which is unstable in the free state, its salt and a strong mineral acid (hydrochloric or sulphuric acid) are practically taken in an amount that is enough for amine salt to be formed, nitrous acid to be isolated from this salt, and the acid medium to be preserved after the process is completed (2.5-3 moles of acid per mole of amine):

$$ArNH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{-}5^\circ C} ArN_2Cl + NaCl + 2H_2O$$

Diazo compounds are almost never isolated in solid form (this is dangerous, because dry diazo compounds are explosive), and a solution is directly used for further transformations. If a solid diazo compound is to be isolated, diazotization is effected in an organic solvent, such as alcohol, using amyl nitrite, $C_5H_{11}ONO$, as a source of nitrous acid and employing acetic acid for acidification. The diazo compound is then precipitated by ether.

Diazo compounds are very reactive substances. Their following properties show that they can exist in several interconverting forms.

Diazo compounds readily dissolve in water. These solutions conduct electric current, i.e., ionic dissociation occurs in the aqueous solution, resulting in the formation of the anion of an acid taken for effecting diazotization (Cl^- in most cases), and the *diazonium ion*, ArN_2^+. Thus, diazo compounds exist as *diazonium salts* in an aqueous solution. Since the solution has a neutral reaction, it should be taken that the diazonium base itself which is contained in the

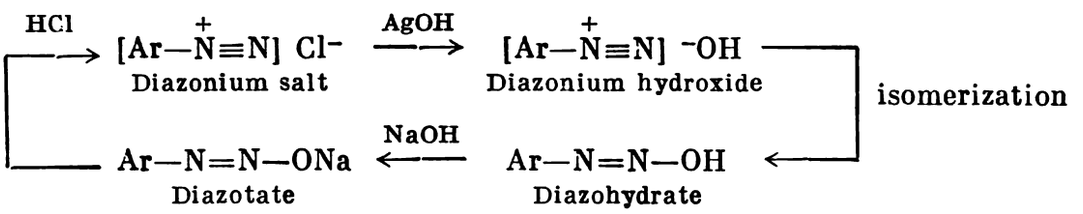
salt possesses clearly-defined basic properties.* This conclusion is borne out by the following experiment. Diazonium hydroxide is formed if a diazonium salt solution is acted on by freshly prepared silver oxide, which contains traces of silver hydroxide:

$$ArN_2Cl + AgOH \longrightarrow ArN_2OH + AgCl$$

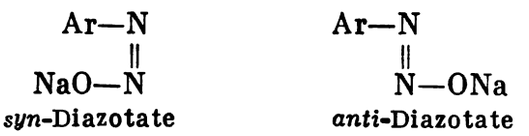
The solution undergoes a strong alkaline reaction, which cannot be caused by AgOH, being a very weak base. The conclusion drawn from this is that diazonium hydroxide, ArN_2OH, formed in this reaction, is a strong base. But the alkaline reaction disappears on its own somewhat later. In this case, the diazo compound does not decompose, as one would expect it to, but is *isomerized*, or transformed into *diazohydrate*, a form which possesses the properties of a weak acid. When alkalies act on diazohydrate, a salt called *diazotate*, ArN_2ONa, is formed, and the residue ArN_2O^- acts as the anion in it. This salt can be reconverted to the initial diazonium salt, ArN_2Cl, if it is acted on by hydrochloric acid.

All these facts do not leave a shadow of doubt that diazo compounds exist in several isomeric forms which are capable of undergoing interconversion. Substances which act in this way are said to be *tautomeric*, while the coexistence of several isomeric forms which are in equilibrium is called *tautomerism*.

Many scientists held different views on the structure of the tautomeric forms of diazo compounds as they were studied down the centuries. The following scheme shows the modern viewpoint on this:



According to Hantzsch's theory, diazotates can exist as two stereoisomers, i.e., *syn*- and *anti*-diazotates:



Reactions of diazo compounds are very diverse. They are usually divided into two groups: reactions with the loss of nitrogen and those without its loss. The former reactions are of great importance

* If the diazonium base were weak, the diazonium salt with a strong acid (e.g., hydrochloric acid) would produce an acid reaction in an aqueous solution as a result of hydrolysis.

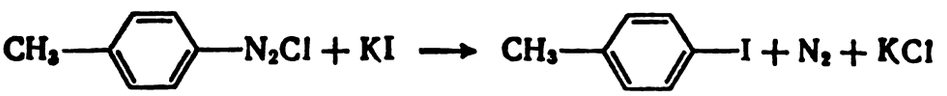
in the synthesis of diverse aromatic compounds, while the latter ones are the basis of an entire industry, i.e., azo dye production.

16.2. Reactions of Diazo Compounds with Nitrogen Loss. The following substitution reactions are the most important reactions of diazo compounds with nitrogen loss.

A diazo group is replaced by a hydroxyl with the formation of phenol when aqueous solutions of diazo compounds are allowed to stand (the reaction occurs more rapidly if they are heated):

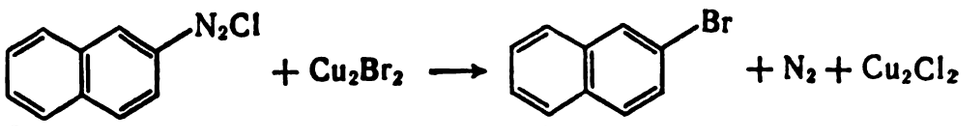
$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + H_2O \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

The diazo group is replaced by iodide under the action of potassium iodide:

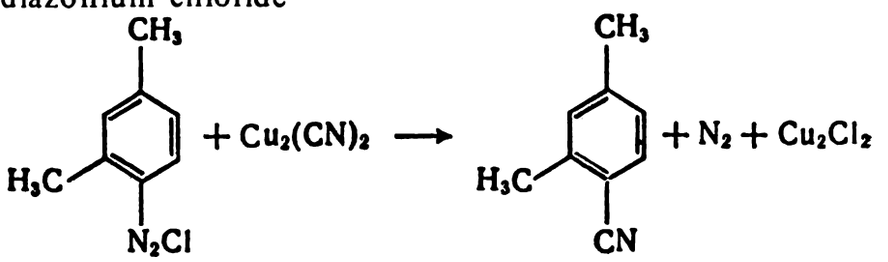


p-Toluene diazonium chloride — *p*-Toluene iodide

The diazo group is replaced by bromide or chloride, and also by the CN group, in the presence of cuprous salts as catalysts (*Sandmeyer's reaction*):



β-Naphthalene diazonium chloride — β-Bromonaphthalene



2,4-Dimethyl benzene diazonium chloride (*m*-xylene diazonium chloride) — 1-Cyano-2,4-dimethyl benzene (*p*-cyano-*m*-xylene)

Water-insoluble diazonium borofluorides precipitate when hydrofluoboric acid, HBF_4, is added to aqueous solutions of diazo compounds:

$$C_6H_5N_2Cl + HBF_4 \longrightarrow C_6H_5N_2 \cdot BF_4 + HCl$$

This reaction is used to isolate diazonium salts from solutions. In addition, borofluorides serve as intermediate products when the diazo group is being replaced by fluorine. The reaction occurs on careful heating:

$$C_6H_5N_2 \cdot BF_4 \longrightarrow C_6H_5F + N_2 + BF_3$$

This reaction is of great importance in obtaining aromatic fluorine derivatives, because fluorine cannot be introduced into the aromatic nucleus by direct halogenation.

Two reactions, i.e., the replacement of the diazo group by an alcohol residue (formation of phenolic esters) and replacement by hydrogen (formation of hydrocarbons), occur simultaneously when alcoholic solutions of diazo compounds are heated:

$$C_6H_5N_2Cl \xrightarrow[-N_2;\ -HCl]{CH_3OH} \begin{cases} \longrightarrow C_6H_5OCH_3 \\ \longrightarrow C_6H_6 \end{cases}$$

The reaction occurs mainly in one direction or another, depending on the nature of an alcohol and on the conditions.

The diazo group can be replaced by hydrogen also under the action of some weak reducing agents (formic acid, hypophosphites).

Organomercury compounds are formed under the action of mercuric chloride and copper powder:

$$C_6H_5N_2Cl + HgCl_2 + 2Cu \longrightarrow C_6H_5HgCl + N_2 + Cu_2Cl_2$$

The diazo group is replaced by antimony, bismuth and tin with the aid of similar reactions. These reactions were discovered by Academician A. N. Nesmeyanov and are widely used in synthesizing various organometallic compounds.

Thiophenols are formed when diazo compounds are treated with potassium hydrosulphide:

$$C_6H_5N_2Cl + KSH \longrightarrow C_6H_5SH + KCl + N_2$$

The diazo group can be replaced also by other groups: the azido group (under the action of sodium azide), the nitro group (under the action of nitrites in the presence of cuprous salts, i.e., under the conditions of Sandmeyer's reaction), the aldehyde group CHO, and phosphorus- and arsenic-containing groups.

Diazonium salts react also with substances which contain conjugated double bonds (*Meerwein's reaction*):

$$C_6H_5N_2Cl + CH_2{=}CH{-}COOH \longrightarrow C_6H_5{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}COOH + N_2$$

All this makes diazo compounds important intermediate products in the synthesis of the most diverse aromatic compounds.

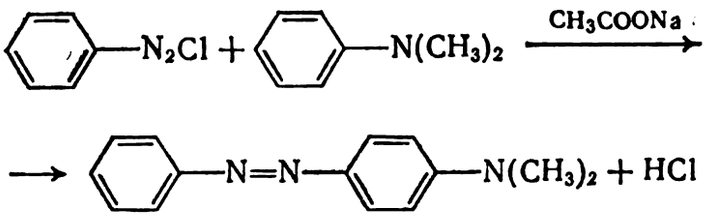
16.3. Reactions of Diazo Compounds without Loss of Nitrogen. One of the reactions which occur without the loss of nitrogen is *hydrazine formation* in the reduction of diazo compounds. This reaction is the basis of the industrial production of *phenylhydrazine*:

$$C_6H_5N_2Cl \xrightarrow{\substack{SnCl_2 \text{ or} \\ NaHSO_3+Zn}} C_6H_5NH{-}NH_2$$

Hydrazine derivatives are used as reagents for the carbonyl group (see Sec. 11.4).

The most important reaction of diazo compounds without the loss of nitrogen is the *azo coupling reaction*, in which the Ar—N=N— group replaces hydrogen of the aromatic nucleus of a phenol or amine, forming hydroxyazo and aminoazo compounds:

$$C_6H_5N_2Cl + C_6H_5OH + NaOH \longrightarrow \underset{\substack{p\text{-Hydroxyazobenzene}}}{C_6H_5{-}N{=}N{-}C_6H_4OH} + H_2O + NaCl$$



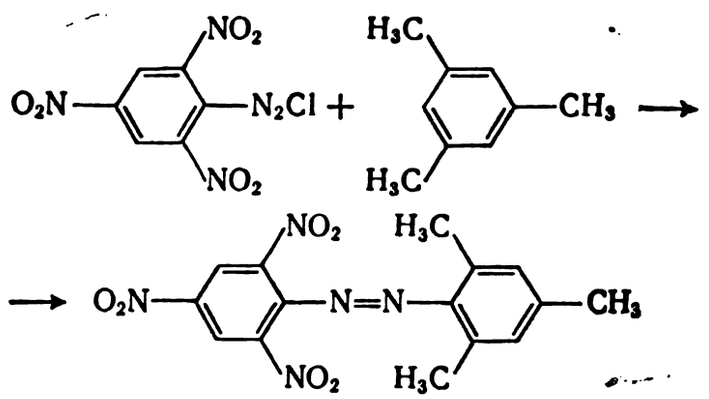
p-Dimethyl aminoazobenzene

By its mechanism, azo coupling is another example of *electrophilic substitution* in the aromatic ring: owing to the positive charge, the diazonium ion, ArN_2^+, acts as an electrophilic particle. But since the diazonium ion has very weak electrophilic properties, it reacts only with aromatic compounds whose nucleus is activated by electron-donating groups: the hydroxyl or the amino group. Aromatic amines or phenols which participate in a reaction are called *azo components*, while the diazo compounds introduced into a reaction are called *diazo components*. The creation of a necessary medium is of great importance in carrying out a reaction; it should be weakly alkaline when phenols are involved, and weakly acidic when amines are involved. This is required for creating the necessary conditions under which azo components can exist in the most active form: phenols as phenoxide ions, $Ar{-}O^-$, and amines as salts that are readily hydrolyzed with the formation of free bases, which are the ones that enter into a reaction.

Azo coupling reactions occur in the *para-* or *ortho*-position towards a hydroxyl or an amino group.

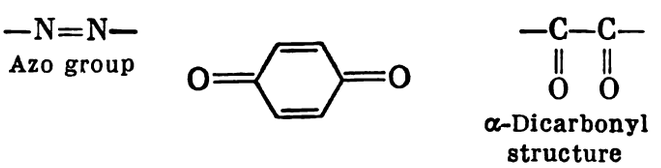
The activity of azo components is the greater, the higher is electron density in their nucleus; therefore, polyhydric phenols (resorcinol, phloroglucinol), polyamines and aminophenols react especially

readily. A diazo compound becomes more active when the aromatic nucleus contains electron-accepting substituents, which help to increase the positive charge of the diazonium ion. Therefore, for instance, diazotized picramide can combine even with the hydrocarbon—mesitylene:



Substances formed by the azo coupling reaction relate to the class of aromatic *azo compounds*. They are characterized by the presence of the —N=N— group. Both free valencies of this group are linked with aromatic radicals. The most interesting feature of azo compounds is that all of them are coloured. Azo compounds of the most diverse colour can be obtained, depending on the structure of the initial azo and diazo components. Many of these substances are capable of attaching themselves to different materials, imparting colour to them. Such substances, known as *azo dyes*, constitute a very broad and diversified (as regards shades), though not the most important (as regards colour quality), class of synthetic dyes.

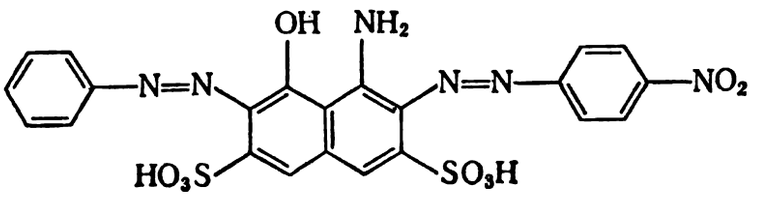
It was noticed as early as the nineteenth century that the molecules of coloured organic substances contain definite atomic groupings, which were termed *chromophores*, e.g.,



Quinoid structure

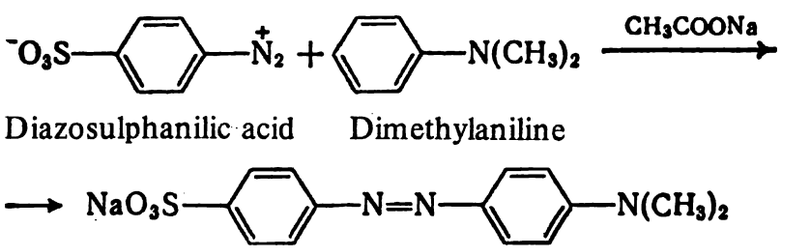
But a coloured substance will be a dye only if it is capable of adhering to a fibre. Organic substances acquire this ability from *auxochromes*, which are strongly polar groups and are, as a rule, either acidic or basic. Amino, carboxyl, sulpho and hydroxyl groups are auxochromes.

An example of azo dyes is Naphthol blue-black B dye, which is used for dyeing woolen fabrics:



In this case, chromophores are azo groups, auxochromes, amino, hydroxyl and sulpho groups. This azo dye can be obtained by the azo coupling of H acid with diazotized aniline and diazotized *p*-nitroaniline.

Many azo dyes are capable of changing their colour in conformity with the pH of a medium, i.e., they are capable of acting as indicators. An example is helianthin (methyl orange), which is obtained from diazosulphanilic acid and dimethylaniline:

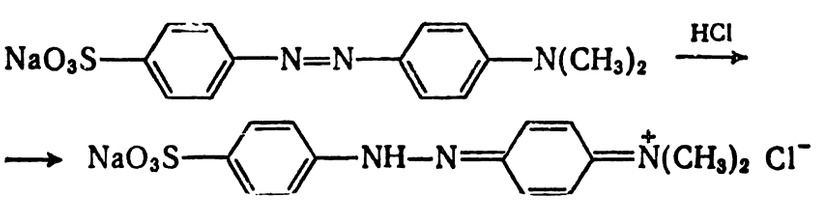


Diazosulphanilic acid Dimethylaniline

4-Dimethylamino-4-azobenzene sodium sulphonate (methyl orange)

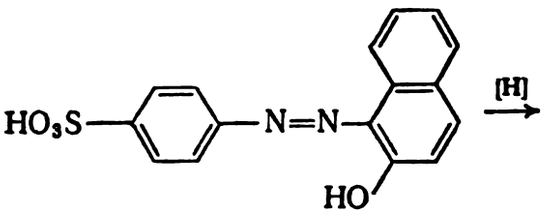
Methyl orange is a brightly coloured substance which is rather well soluble in water. Its colour changes in conformity with the medium: it is yellow in alkaline and neutral media, and red in an acid medium. Owing to this property, methyl orange is widely used as an acid-base indicator in analytical chemistry.

The colour of methyl orange changes under the action of acids, because one of the benzene nuclei passes over to the *quinoid* form:

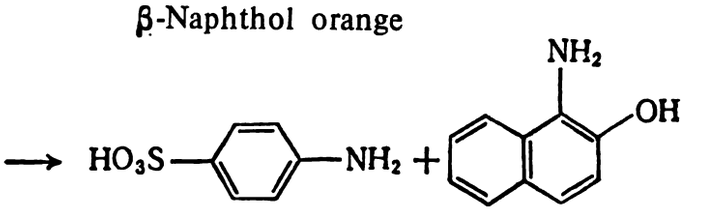


Azo dyes (and azo compounds in general) are capable of being split along the —N=N— bond under the action of strong reducing agents (stannous chloride, sodium hydrosulphite), and amino groups

are formed at the site of rupture:



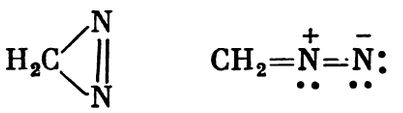
β-Naphthol orange



Sulphanilic acid 1-Amino-2-naphthol

The reaction is used for obtaining some amino compounds and ascertaining the structure of azo dyes.

16.4. Aliphatic Diazo Compounds. The simplest and the most important representative of aliphatic diazo compounds is diazomethane, CH_2N_2. Aliphatic diazo compounds are quite different from aromatic ones by their properties and structure. The formula with a three-membered ring I was formerly ascribed to them. But electron-diffraction studies have shown that the diazomethane molecule has a linear structure II:



I II

Diazomethane is obtained by decomposing several compounds which contain the $CH_3-\underset{|}{N}-NO$ grouping, e.g., by the action of alkali on N-methyl-N-nitrosoacetamide:

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-NO+NaOH \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-ONa+CH_2N_2+H_2O$$

Diazomethane is a yellow gas which boils at —24°C; it is extremely dangerous, because it is toxic and explosive. It is usually used as a solution in diethyl ether. Since diazomethane is highly reactive, many reactions involving it can be carried out under mild conditions. It acts as a *methylating agent* on substances of an acidic nature:

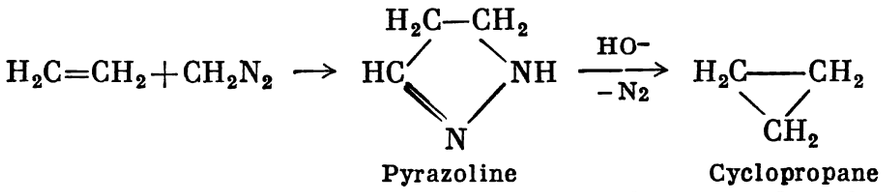
$$CH_3COOH+CH_2N_2 \longrightarrow CH_3COOCH_3+N_2$$

$$C_6H_5OH+CH_2N_2 \longrightarrow C_6H_5-OCH_3+N_2$$

Of course, there is no need to methylate acetic acid or phenol by diazomethane, as this can be done by other methods which are more

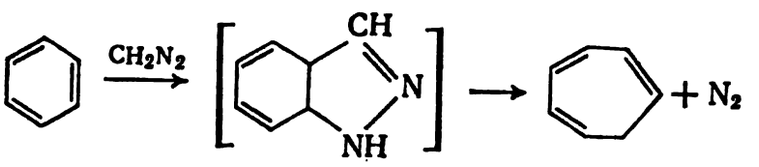
simple. But diazomethane is an ideal agent for methylating compounds which decompose on heating or under the action of acids.

Another interesting ability of diazomethane is that it can react with compounds containing multiple bonds. For example, diazomethane and ethylene form the cyclic nitrogen-containing compound, *pyrazoline*, which gives cyclopropane after decomposition:

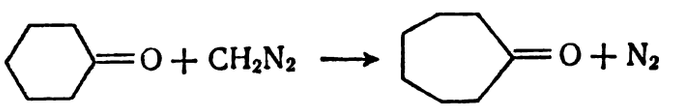


Pyrazoline Cyclopropane

Benzene also acts like compounds which have a double bond, forming *cycloheptatriene* as it interacts with diazomethane, i.e., the ring expands:

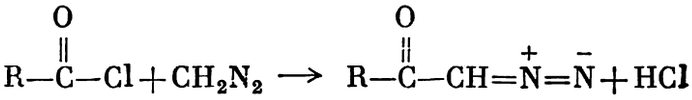


The reaction with cyclic ketones likewise occurs with ring expansion:

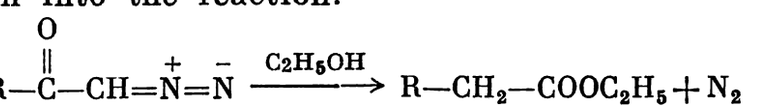


Cyclohexanone Cycloheptanone (suberone)

Diazoketones are formed when diazomethane acts on acid chlorides:



When heated together with alcohol, diazoketone forms an ester, which, in the acid radical, has one carbon atom more than the acid chloride taken into the reaction:



Diazomethane can thus be used to elongate the carbon chain of carboxylic acids (*Arndt-Eistert synthesis*).

There are also other representatives of the aliphatic diazo compound series, but they are not of great significance. *Ethyl diazoacetate*, $C_2H_5OCOCHN_2$, is of certain importance, being more stable than diazomethane; in particular, it can be distilled under vacuum and even at atmospheric pressure (b.p. 145°C). It enters into the same reactions as diazomethane.

Chapter 17

ORGANOELEMENT COMPOUNDS

Organic compounds with a direct element-carbon bond have the common name of *organoelement compounds.*

17.1. General Characteristics of Organoelement Compounds. Besides the "organogen" elements (C, H, O, N, S, Cl, Br, I, P), organic molecules can have many other chemical elements in their composition.

These compounds are classified above all by the element which they contain. Organic derivatives of elements belonging to the same group of the periodic system have similar properties, and therefore they can be combined and considered together. That is how the natural classification of organoelement compounds by groups of the periodic system originates.

Depending on the structure, organoelement compounds can be *ordinary* ones, where all the valencies of an element are spent on bonding with carbon atoms, and *mixed* ones, where only a part of the valencies of an element is linked with carbon, while the rest of them are spent on the bonding with oxygen, sulphur, nitrogen and halogens.

This is exemplified by the following compounds:

Ordinary organoelement compounds		Mixed organoelement compounds	
C_4H_9Li . .	Butyllithium	CH_3MgI	Methylmagnesium iodide
$(CH_3)_2Zn$ . .	Dimethyl zinc	$CH_3P(OH)_2$ ‖ O	Methylphosphonic acid
$(CH_3)_3P$ . .	Trimethylphosphine	CH_3AsCl_2	Methyldichloroarsine
$(C_6H_5)_5P$ . .	Pentaphenyl phosphorane		

Organoelement compounds include *organometallic compounds*, which have one common feature: carbon in the carbon-metal bond constitutes the *negative* end of the dipole, unlike the above-mentioned C—X bonds (X stands for a halogen, O, N, S, etc.), where polarization occurs in the opposite direction. It is the presence of a partial negative charge on carbon that determines the peculiar features of organometallic compounds, i.e., their ability to enter into

electrophilic and not nucleophilic reactions, being characteristic of the bonds with $C^{\delta+}—X^{\delta-}$ polarization. This difference is clearly seen, for example, when water acts on methyl iodide and methyl sodium:

$$\overset{\delta+}{CH_3}—\overset{\delta-}{I}+\overset{\delta+}{H}—\overset{\delta-}{O}—\overset{\delta+}{H} \longrightarrow CH_3—OH+HI$$

$$\overset{\delta-}{CH_3}—\overset{\delta+}{Na}+\overset{\delta+}{H}—\overset{\delta-}{O}—\overset{\delta+}{H} \longrightarrow CH_4+NaOH$$

17.2. Organomagnesium Compounds. These compounds are often called *Grignard reagents*, while syntheses carried out with their aid are termed *Grignard reactions* in honour of the French scientist Victor Grignard, who was the first to study organomagnesium compounds.

To obtain organomagnesium compounds, the turnings of metallic magnesium are covered with anhydrous (absolute) ether and a halogen derivative, such as methyl iodide, is gradually added to this mixture. In the course of the reaction, magnesium gradually passes into solution. The process occurs according to the scheme:

$$R—X+Mg \longrightarrow R—Mg—X$$

Ether is not a simple solvent in this reaction. It forms, with organomagnesium compounds, complexes of the $RMgX \cdot 2(C_2H_5)_2O$ composition that are called *etherates*.

The structure of the Grignard reagent has been the subject of much controversy for many years, but their reactions are quite satisfactorily expressed by an ordinary formula of mixed organomagnesium compounds (alkylmagnesium halides), RMgX.

Organomagnesium compounds are not separated from solutions in which they are obtained; syntheses are carried out by adding the second component to these solutions. Atmospheric oxygen readily oxidizes organomagnesium compounds, but oxidation is prevented by means of ethereal vapours, which force out air.

Being typical representatives of organometallic substances, organomagnesium compounds have the corresponding $C^{\delta-}—Mg^{\delta+}$ bond polarization. This is expressed in the ability to enter into substitution (scheme 1) and addition reactions (scheme 2):

$$\overset{\delta-}{R}—\overset{\delta+}{Mg}—X+\overset{\delta+}{A}—\overset{\delta-}{B} \longrightarrow R—A+B—Mg—X \qquad (1)$$

$$\overset{\delta-}{R}—\overset{\delta+}{Mg}—X+\overset{\delta+}{A}=\overset{\delta-}{B} \longrightarrow R—A—B—Mg—X \qquad (2)$$

The most important reactions of organomagnesium compounds are the following:

1. Organomagnesium compounds with water form hydrocarbons:

$$\overset{\delta-}{CH_3}—\overset{\delta+}{Mg}—\overset{\delta+}{I}+\overset{\delta+}{H}—\overset{\delta-}{O}—\overset{\delta+}{H} \longrightarrow CH_4+Mg(OH)I$$

This is an example of a substitution reaction in which the carbon atom, which bears a partial negative charge, combines with hydrogen, i.e., with the positive end of the dipole, which is in water.

Reactions with other compounds which contain mobile hydrogen, particularly with alcohols, acids and amines, occur similarly:

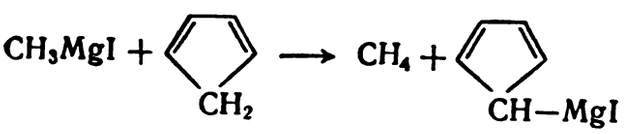
$$CH_3MgI + CH_3OH \longrightarrow CH_4 + CH_3OMgI$$
$$C_6H_5MgBr + CH_3COOH \longrightarrow C_6H_6 + CH_3COOMgBr$$
$$C_6H_5CH_2MgCl + C_3H_7NH_2 \longrightarrow C_6H_5CH_3 + C_3H_7NHMgCl$$

In these reactions, a salt-like magnesium compound of no practical importance is formed together with the hydrocarbon.

This reaction is used in analytical chemistry, being the basis of the *method of determining active hydrogen by the Chugaev-Tserevitinov reaction*. The methylmagnesium iodide solution, CH_3MgI, is used as a reagent. One mole of methane is isolated per equivalent of active hydrogen when reactions are carried out with organic compounds containing mobile hydrogen (alcohols ROH, amines RNH_2 and RNHR). The number of hydroxyl or amino groups contained in a given substance can be calculated by measuring the volume of methane evolved under the action of excess CH_3MgI and knowing the weighed portion of the hydroxyl- or amino-containing substance.

2. Reactions with mobile hydrogen attached to the carbon atom occur by the same general scheme as the reaction considered above. But of certain interest in this case is magnesium-containing products, e.g.,

$$\underset{\text{Acetylene}}{2CH_3MgI + CH{\equiv}CH} \longrightarrow \underset{\text{Iotsich reagent}}{2CH_4 + IMg{-}C{\equiv}C{-}MgI}$$

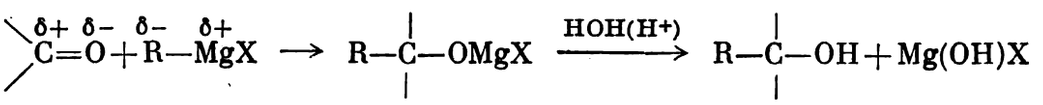


Cyclopentadiene — Cyclopentadienyl magnesium iodide

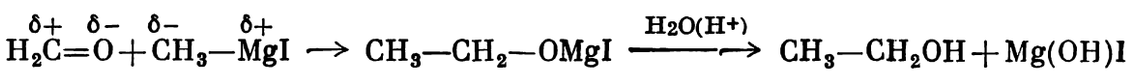
Compounds obtained in such reactions contain magnesium which is linked with carbon. They are real organomagnesium compounds which enter into all the reactions characteristic of them.

3. Addition of organomagnesium compounds to polarized multiple bonds. The addition to carbonyl compounds with the formation of alcohols is of the greatest interest. The hydrocarbon radical R, which bears a partial negative charge in an organomagnesium compound, acts as a nucleophilic reagent in this reaction, being added to carbonyl carbon, while the magnesium halide combines with

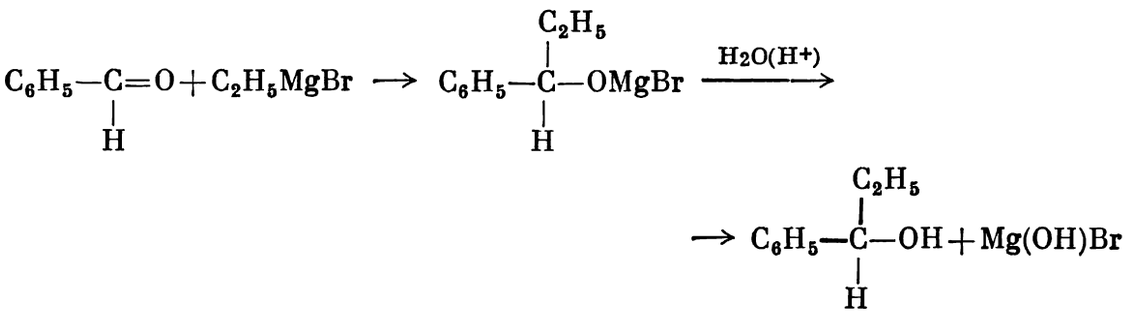
oxygen:



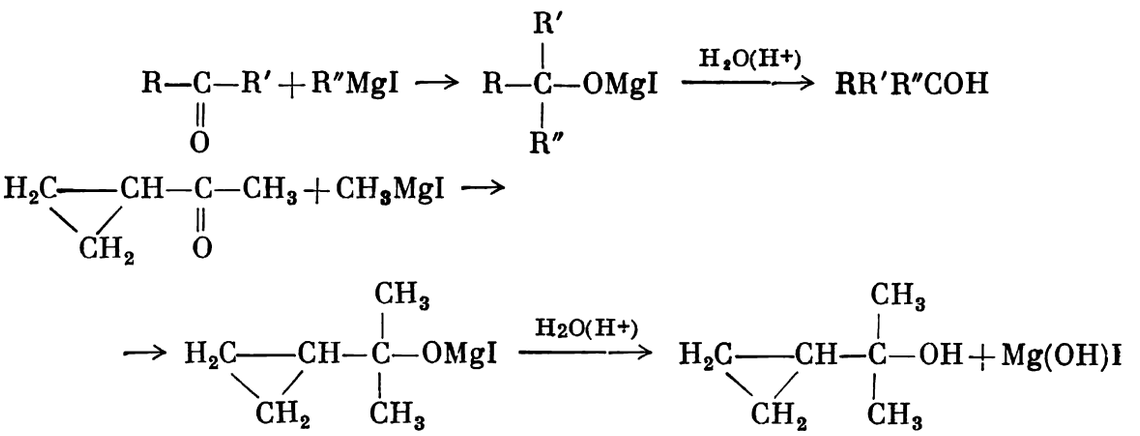
Alcohols of different structures can be obtained, depending on the nature of a carbonyl compound used in a reaction. *Primary alcohols* are obtained from formaldehyde



secondary alcohols are formed from other aldehydes



and *tertiary alcohols*, from ketones:



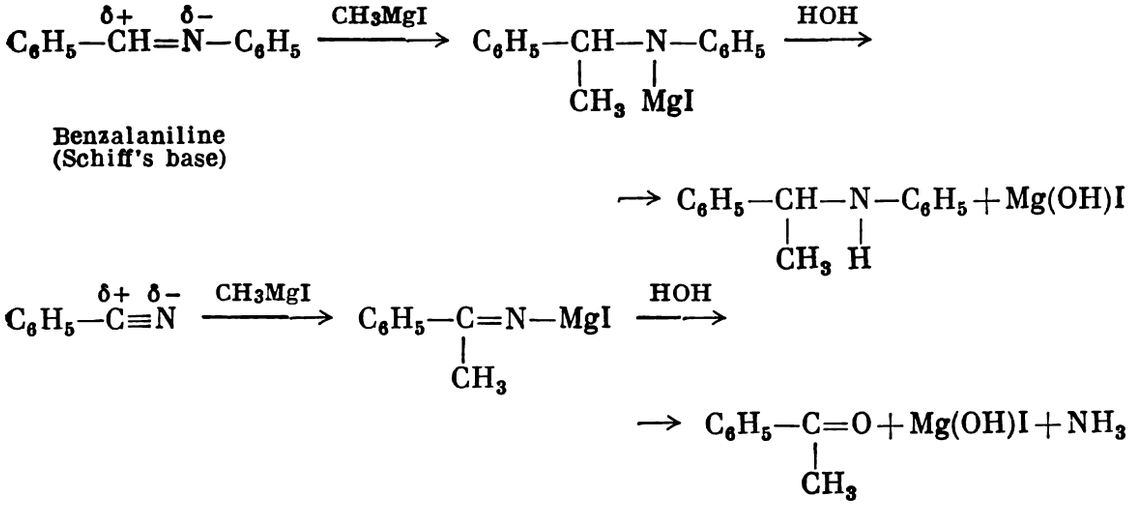
The given examples show that alcohols thus obtained can contain aliphatic, cyclic and aromatic radicals in their composition.

In these syntheses, organic compounds of lithium and sodium can be used instead of organomagnesium compounds.

Carbon dioxide, O=C=O, can also act as a carbonyl compound. When organomagnesium compounds react with it, they form salts of carboxylic acids, which can then be transformed into the corresponding acids:

Substances having multiple bonds $\diagdown\!\!\diagup C{=}N-$ and $-C{\equiv}N$ also interact according to this type of reactions; amines are obtained in

the first case, and ketones, in the second:



Benzalaniline
(Schiff's base)

4. Organomagnesium compounds react with halogen derivatives according to the type of Würtz reaction, forming hydrocarbons:

$$CH_2{=}CH{-}CH_2I + CH_3MgI \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 + MgI_2$$

Alcohols, ketones and acids obtained by the Grignard reaction can serve as initial substances for synthesizing many other organic compounds. This determines the importance of organomagnesium compounds in organic synthesis.

Before organomagnesium compounds were discovered, organozinc compounds were widely used for alcohol synthesis. Syntheses with the aid of organozinc compounds were worked out by A. M. Butlerov and his pupils. In these syntheses, ordinary organozinc compounds of the R_2Zn composition were used.

In 1864, Butlerov synthesized the first representative of the tertiary alcohol series, trimethylcarbinol, by using the reaction between dimethyl zinc and acetyl chloride. Another reaction of organozinc compounds used by Butlerov's school gives hydrocarbons:

$$(CH_3)_3Cl + (C_2H_5)_2Zn \longrightarrow (CH_3)_3C{-}CH_2{-}CH_3 + C_2H_5ZnI$$

2,2-Dimethylbutane
(neohexane)

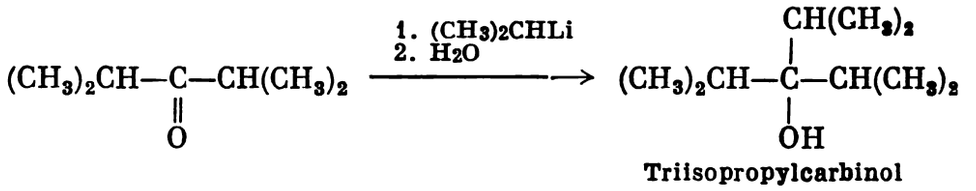
Compounds of lithium, sodium and potassium enter into the same reactions as organomagnesium compounds. But since these compounds are extremely sensitive to atmospheric oxygen (they inflame spontaneously) and moisture, it is less convenient to work with organic compounds of alkali metals than with organomagnesium ones. Therefore, they are used only when compounds with heightened reactivity are required.

Organic compounds of alkali metals are very active chemically, because their carbon-metal bond is of an ionic nature. The carbanions of the type CH_3^-, $C_6H_5^-$, and others, participate in the reactions of these compounds. The activity of organic compounds of alkali

metals increases for individual metals in the following order:

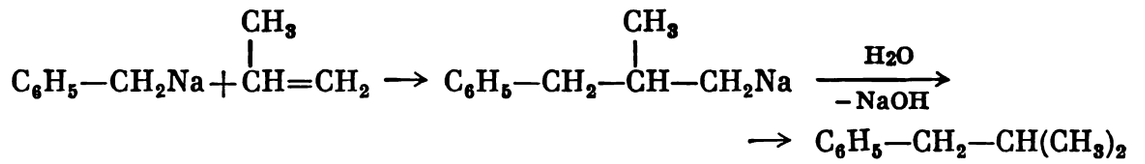
$$Li < Na < K < Rb < Cs$$

Organolithium compounds are used for synthesizing greatly branched alcohols, which cannot be obtained by organomagnesium synthesis, e.g.,



Triisopropylcarbinol

The heightened reactivity of organic compounds of alkali metals is exhibited also in their ability to be added along double carbon-carbon bonds:



17.3. Organoaluminium Compounds. Trialkylaluminium compounds, R_3Al, were known as early as the nineteenth century. But interest was taken in them only when the German chemist Ziegler discovered a simple direct method of obtaining them from metallic aluminium, hydrogen and ethylene hydrocarbons (1955):

$$2Al + 3H_2 + 6C_2H_4 \xrightarrow{100°C;\ 80\ kg/cm^2} 2(C_2H_5)_3Al$$

The simplest aluminium trialkyls are liquids which inflame spontaneously in air and must be handled in an inert atmosphere (nitrogen).

In the last two decades, organoaluminium compounds have turned from very rare "exotic" substances into extremely important products of modern technology. This field is continuing to develop rapidly, and hundreds of patents on the methods of obtaining and using organoaluminium compounds are being given out. The Ziegler reaction is used for industrially synthesizing aluminium trialkyls:

$$2Al + 3H_2 + 6C_nH_{2n} \longrightarrow 2(C_nH_{2n+1})_3Al$$

Compounds of the type $RAlCl_2$ and R_2AlCl are formed when alkyl halides act on metallic aluminium in an autoclave:

$$3RCl + 2Al \longrightarrow RAlCl_2 + R_2AlCl$$

Aluminium trialkyls have become important in several fields. They are used as catalysts of polymerization processes. Low-pressure polyethylene and other polyolefins, and butadiene and isoprene rubbers are obtained with their aid.

Higher aluminium trialkyls are obtained for synthesizing higher alcohols from ethylene and triethylaluminium:

$$(C_2H_5)_3Al + 12CH_2{=}CH_2 \longrightarrow (C_{10}H_{21})_3Al$$

These aluminium trialkyls are converted by oxidation by atmospheric oxygen into aluminium alkoxide, which is decomposed by water into aluminium hydroxide and higher alcohol:

$$(C_{10}H_{21})_3Al \xrightarrow{O_2} (C_{10}H_{21}O)_3Al \xrightarrow{H_2O} C_{10}H_{21}OH$$

Higher alcohols are used for obtaining flotation reagents, which are employed in the concentration of ores of nonferrous metals; they are also used for producing synthetic detergents and for many other important purposes.

Higher fatty acids are obtained from aluminium trialkyls:

$$(C_{10}H_{21})_3Al \xrightarrow{CO_2} (C_{10}H_{21}COO)_3Al \xrightarrow{H_2O} C_{10}H_{21}COOH$$

These acids are also used for producing detergents. Unlike acids obtained in paraffin oxidation, acids synthesized with the aid of organoaluminium compounds have an *unbranched* chain, like those which are in the composition of fats. In the future, this may be important in the synthesis of food fats.

Diagram 17.1 shows the use of aluminium trialkyls in greater detail.

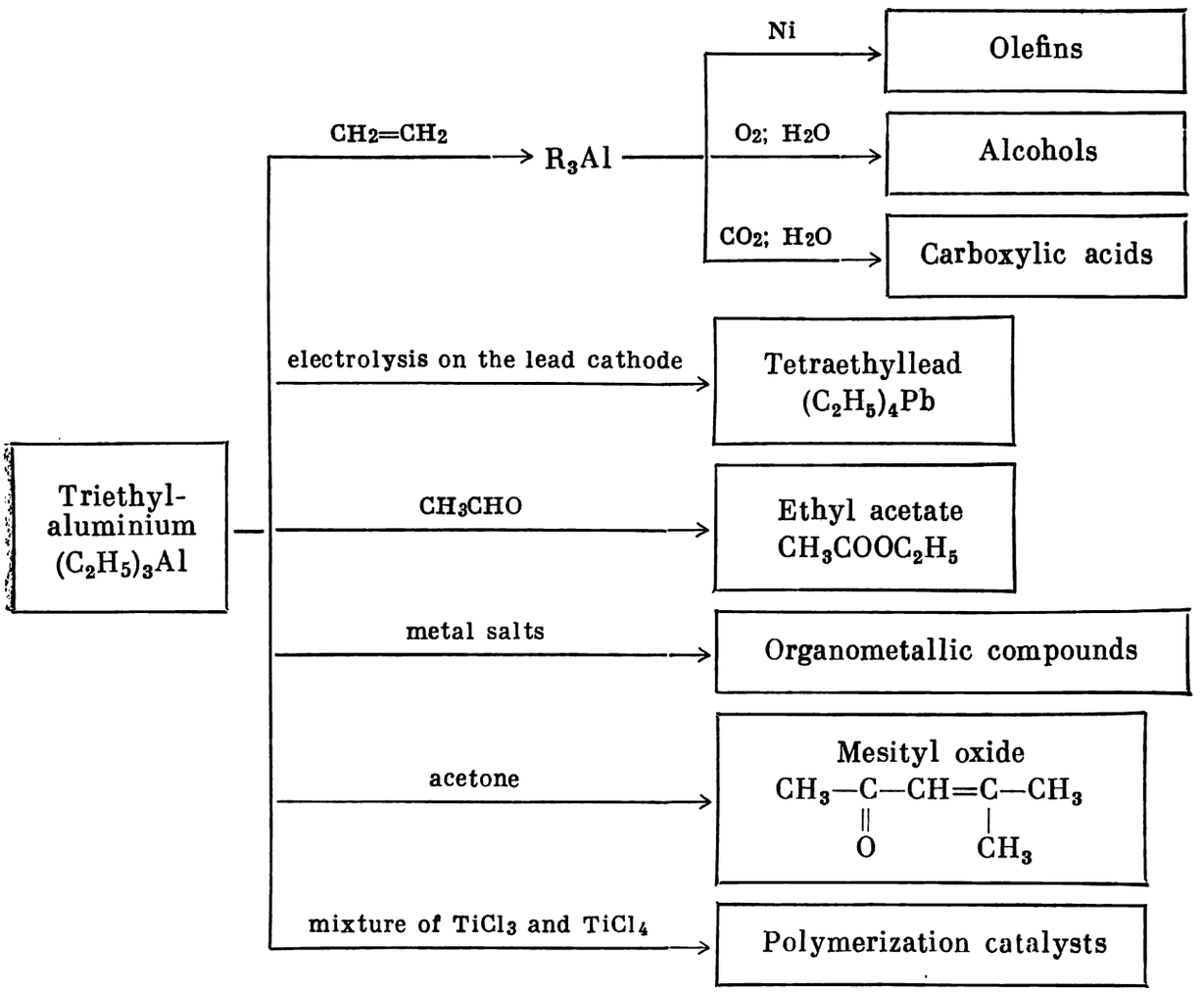
17.4. Organometallic Compounds of Transition Metals. Transition metals are the elements of the periodic table in which there is a partially filled *d*-shell. These metals have atomic numbers of 21-30 (from scandium to zinc), 39-47 (from yttrium to silver), and 71-80 (from lutecium to mercury). Many of these elements form organic compounds of an unusual structure.

An example of such compounds is dicyclopentadienyliron or *ferrocene*. It has the composition of $C_{10}H_{10}Fe$ and consists of orange crystals; it melts at 174°C. Ferrocene boils without decomposition at 250°C, and dissolves in organic solvents. It can be obtained by passing cyclopentadiene vapours over iron powder at 300°C:

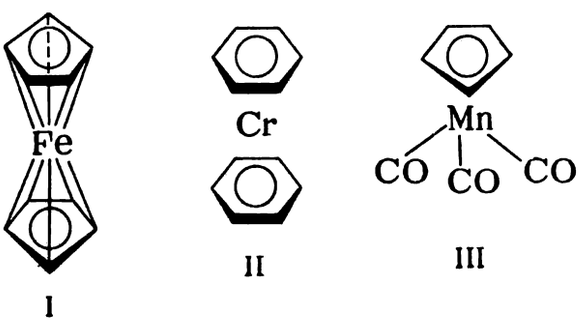
$$C_5H_6 \xrightarrow{Fe} (C_5H_5)_2Fe$$

Ferrocene possesses the properties of an aromatic compound: it acylates by the Friedel-Crafts reaction, sulphonates, and does not decompose when heated with concentrated HCl or 10-percent NaOH solution. Its properties are unusual for an organometallic

DIAGRAM 17.1. **Use of Aluminium Trialkyls**



compound because of a peculiar structure (formula I).



I II III

Structures of such a type have become known as "sandwich" structures; in this case, an iron atom lies between the two cyclopentadienyl rings. Such a structure of ferrocene has been confirmed by X-ray diffraction analysis and by spectral data.

A. N. Nesmeyanov and his pupils have made a great contribution to the investigation of ferrocene and its derivatives.

There are ferrocene analogues which contain cobalt or nickel instead of iron, being known as *cobaltocene* and *nickelocene*. *Dibenzenechromium* (formula II) has a similar sandwich structure.

Cyclopentadienylmanganese tricarbonyl (formula III) is used as an antidetonation additive for raising the octane number of fuel. It is less poisonous than tetraethyl lead. But tetraethyl lead (see Sec. 8.1) has lost none of its importance as an antidetonation additive.

17.5. Organosilicon Compounds. In the periodic table of the elements, silicon, like carbon, is in the fourth group and is situated directly under carbon. But the compounds of both elements are far less similar than is expected from their close arrangement in the periodic table of the elements. Considerably great differences between carbon and silicon compounds are seen even from a comparison of the properties of the simplest compounds of both elements, e.g., the properties of CO_2 and SiO_2, H_2CO_3 and H_2SiO_3, CH_4 and SiH_4. Organic silicon compounds are structurally similar to carbon compounds (both elements are tetravalent), but they considerably differ by their properties.

The first two members of the homologous series of silicohydrides (*silanes*), SiH_4 and Si_2H_6, are gases, and the subsequent ones are liquids. All of them have an unpleasant odour and are poisonous, and they mix with organic solvents. One of the methods of obtaining silanes is by the action of acids or alkalies on metal silicides, e.g.,

$$Mg_2Si + 4HCl \longrightarrow SiH_4 + 2MgCl_2$$

Silanes, unlike hydrocarbons, are compounds of low stability, i.e., they ignite in the air and are readily hydrolyzed by water:

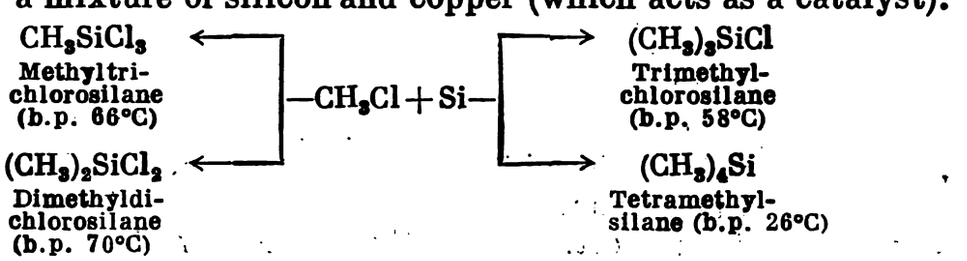
$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$
$$Si_2H_6 + 4H_2O \longrightarrow 2SiO_2 + 7H_2$$

Compounds in which hydrocarbon radicals instead of hydrogen are linked with silicon atoms possess higher stability.

There are silicon analogues of hydrocarbons, halogen derivatives, alcohols, ethers, etc. Alkyl and aryl silanes or their halogen derivatives are obtained with the aid of organomagnesium compounds:

$$SiCl_4 \xrightarrow{CH_3MgI} CH_3SiCl_3 \xrightarrow{CH_3MgI} (CH_3)_2SiCl_2 \xrightarrow{CH_3MgI} (CH_3)_3SiCl \xrightarrow{CH_3MgI} (CH_3)_4Si$$

Another method is used industrially for synthesizing such compounds; halogen derivatives, say methyl chloride, are passed at 300-350°C over a mixture of silicon and copper (which acts as a catalyst):



Tetramethylsilane is a representative of totally alkylated silicon compounds. It is a readily boiling liquid and is similar to paraffin hydrocarbons by its chemical inertness.

Alkylchlorosilanes are characterized by their ability to be readily hydrolyzed, being similar to silicon tetrachloride in this respect:

$$(CH_3)_3SiCl \xrightarrow[-HCl]{H_2O} (CH_3)_3SiOH$$

Trimethyl silanol

Alcoholic analogues called *silanols*, which are formed in hydrolysis, are unstable and, as water is eliminated, readily pass into *siloxanes*, which are organosilicon analogues of ethers:

$$2(CH_3)_3SiOH \xrightarrow[-H_2O]{} (CH_3)_3Si{-}O{-}Si(CH_3)_3$$

Hexamethyl disiloxane

Dialkyldichlorosilanes are hydrolyzed similarly, but polymeric compounds are formed in this case. Dialkyldichlorosilanes are used for obtaining organosilicon polymers (see Sec. 23.10).

Silicon, like carbon, is capable of forming chains and rings. For instance, there are *hexamethyl disilane* $(CH_3)_3Si{-}Si(CH_3)_3$, a liquid which boils at 112-114°C, and its higher homologues, which contain up to nine silicon atoms in a chain. These substances are oxidized and hydrolyzed rather readily with a cleavage of the Si—Si bonds.

17.6. Organophosphorus Compounds. Phosphorus is an element of the fifth group of the periodic table, and it is a nitrogen analogue. There is a definite similarity between the organic derivatives of these elements, e.g.,

$R{-}NH$	$R{-}PH_2$
Primary amines	Primary phosphines

Like the corresponding nitrogen compounds, there are secondary and tertiary phosphines, and also analogues of quaternary ammonium compounds: phosphonium salts. Phosphines, like amines, are bases which with acids can yield salts:

$$\underset{\text{Methyl-phosphine}}{CH_3PH_2} + HCl \rightleftarrows \underset{\text{Methylphosphonium chloride}}{[CH_3PH_3]^+Cl^-}$$

But the basic properties of phosphines are considerably weaker than those of amines.

Phosphorus compounds differ from nitrogen ones mainly by the ability of phosphines to readily react with the elements which have great affinity for electrons (halogens, oxygen). This is because the free electron pair of phosphines and of other compounds of trivalent phosphorus is more remote from the nucleus than in nitrogen. The more remote is an electron from the nucleus, the less is it attracted

by the nucleus and the more readily can it pass over to another atom. For example, phosphines are readily oxidized with the formation of the corresponding oxides (in the air, the simplest phosphines inflame spontaneously). When primary and secondary phosphines are being oxidized, alkylphosphonic acid and dialkylphosphinic acid are formed respectively, while oxides are obtained from tertiary phosphines:

$$RPH_2 \xrightarrow{[O]} R{-}P(OH)_2 \quad (R{-}P(=O)(OH)_2)$$

Alkylphosphonic acid

$$R_2PH \xrightarrow{[O]} R_2P{-}OH \quad (R_2P(=O)OH)$$

Dialkylphosphinic acid

$$R_3P \xrightarrow{[O]} R_3P{=}O$$

Phosphine oxide

The compounds are formed also from chlorophosphines. Chlorophosphoranes are obtained when chlorine is added to the latter, and they are hydrolyzed under the action of water:

$$RPCl_2 \xrightarrow{Cl_2} RPCl_4 \xrightarrow{H_2O} R{-}P(OH)_2 \quad (R{-}P(=O)(OH)_2)$$

$$R_2PCl \xrightarrow{Cl_2} R_2PCl_3 \xrightarrow{H_2O} R_2P{-}OH \quad (R_2P(=O)OH)$$

The foregoing formulas of alkylphosphonic and dialkylphosphinic acids, and also phosphine oxides, contain pentacovalent phosphorus. Does this not contravene the octet rule? Could it be that these compounds, like oxides of amines and their analogues, also contain tetravalent phosphorus, while oxygen is linked by a semipolar bond?

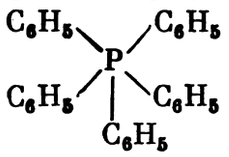
This was thoroughly studied. The measurements of the lengths of bonds and dipole moments have shown that the bonds between phosphorus and oxygen in alkylphosphonic and dialkylphosphinic acids are *intermediate* between single and double bonds, i.e., their true state is *mesomeric* between the extreme structures:

$$R{-}P(=O)(OH)(OH) \longleftrightarrow R{-}P^{+}(O^{-})(OH)(OH)$$

$$(CH_3)_3P{=}O \longleftrightarrow (CH_3)_3P^{+}{-}O^{-}$$

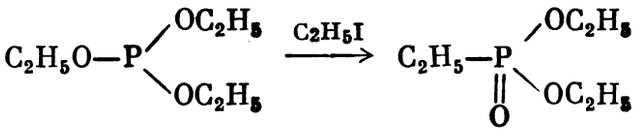
Thus, formulas with pentacovalent phosphorus only approximately show the structure of these compounds.

There are compounds in which phosphorus undoubtedly forms five perfectly the same covalent bonds, e.g., *pentaphenyl phosphorane*, which was first obtained by Wittig (1949):



Pentaphenyl phosphorane possesses characteristic properties of a covalent compound: it dissolves in organic solvents and does not dissolve in water, and has a rather low melting point. G. A. Razuvaev's investigations have shown that all the five phosphorus bonds in this compound are equivalent.

An important reaction for obtaining compounds with the carbon-phosphorus bond was discovered by A. Ye. Arbuzov:



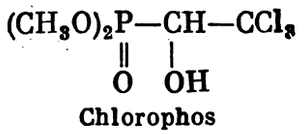
Triethyl phosphite — Diethyl ethylphosphonate

This transformation is known as *Arbuzov's rearrangement*. Initial phosphites are readily obtained from primary alcohols and phosphorus trichloride:

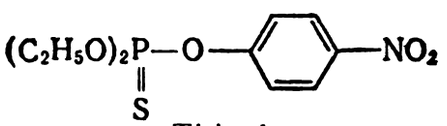
$$PCl_3 + 3C_2H_5OH \longrightarrow P(OC_2H_5)_3 + 3HCl$$

Organophosphorus compounds include a large number of substances which have a strong physiological effect. Therefore, organic phosphorus compounds are used as insecticides and medicinals, and are also poisonous substances in warfare.

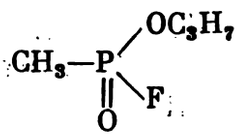
Chlorophos is an insecticide whose effect ranges widely. It is less toxic for animals and man. *Thiophos* is an insecticide which has a contact effect:



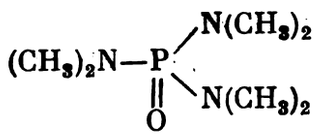
Chlorophos



Thiophos



Sarin



Hexametapol

Fluorophosphonate, or *sarin*, is a poisonous substance which paralyzes the nerves, and its fatal concentration in air is 0.03 mg/lit. Tris(dimethylamido)phosphate is a liquid (b.p. 233°C, m.p. 5-7°C, d^{20} 1.027), and it is used as a polar solvent known by the name of *Hexametapol*.

PART III

HETEROFUNCTIONAL COMPOUNDS

Substances whose molecule contains two or more different functional groups (functions) are known as compounds with heterogeneous (mixed) functions or *heterofunctional compounds*. Such substances deserve special attention for many reasons. It is these compounds which are the most convenient models for considering several general theoretical problems of organic chemistry: the problems of the mutual effect of functional groups, tautomerism, and stereoisomerism. Many practically important substances are heterofunctional compounds.

III.1. Nomenclature of Heterofunctional Compounds. In modern international nomenclature, the names of heterofunctional compounds are composed on the basis of the names of monofunctional compounds (systematic or rational) with the addition of a prefix, which characterizes the additional function.

Thus, apart from the well-known suffix notations (ol, one, al, etc.), functions also have other, prefix, notations (Table III.1). The square bracket, which separates carbon from the rest of the function in Table III.1, indicates that the carbon of the functional group is in the total number of atoms of the carbon skeleton when a given name is being composed. If there is no such bracket, the entire function (including its carbon atom) is considered as a substituent when a name is being composed. For example, hydroxy acid HO—CH_2—CH_2——CH_2—COOH can be called 4-*hydroxybutanoic acid* or 3-*hydroxypropane carboxylic acid*. Accordingly, H_2N—CH_2—CH_2—CH_2—CH_2——CN is 5-*aminopentane nitrile*, 4-*aminobutane carbonitrile* or 4-*cyanobutylamine*.

The main chain is so selected that it necessarily includes the main function and the maximum number of other existing functions. The chain length is unimportant in this respect. The numeration is always so made that the main function would have the lowest number. In Table III.1, functions are given in the order of diminishing seniority.

The greater part of heterofunctional compounds discussed further consists of acids which contain different additional functions. The main function of all these compounds is the carboxyl function, and therefore their names are composed on the basis of rational or syste-

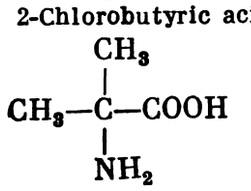
TABLE III-1. **Function Notations**

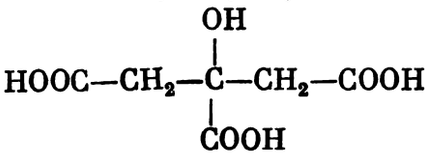
Class of compounds	Functional group	Notation	
		prefix	suffix
Groups mentioned both in the prefix and in the suffix			
Carboxylic acids	—COOH	Carboxy-	-carboxylic acid
	—C(=O)OH	—	-oic acid
Sulpho acids	SO_3H	Sulpho-	-sulphonic acid
Nitriles	—C≡N	Cyano-	-carbonitrile
	—C≡N	—	-nitrile
Aldehydes	—CHO	Formyl-	-carboxaldehyde
	—C(=O)H	Oxo-	-al
Ketone	>C=O	Oxo-	-one
Alcohols, phenols	—OH	Hydroxy-	-ol
Thiols	—SH	Mercapto-	-thiol
Amines	$—NH_2$	Amino-	-amine
Groups mentioned only in the prefix			
Halogen derivatives	F, Cl, Br, I	Fluoro-, chloro-, bromo-, iodo-	—
Nitroso compounds	—NO	Nitroso-	—
Nitro compounds	$—NO_2$	Nitro-	—
Azides	$—N_3$	Azido-	—
Diazo compounds	$—N_2—$	Diazo-	—
Ethers	—OR	Alkoxy-	—

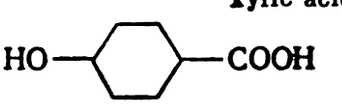
matic names of carboxylic acids, e.g.,

$CH_3—CH_2—CHCl—COOH$
2-Chlorobutyric acid

$HOCH_2—CH_2—CH_2—COOH$
4-Hydroxybutyric acid


2-Amino-2-methyl-propanoic acid


2-Hydroxy-1,2,3-propane tricarboxylic acid (citric acid)


4-Hydroxycyclohexane carboxylic acid

Chapter 18

HALOGEN-SUBSTITUTED ACIDS. HYDROXY ACIDS. ALDEHYDO AND KETO ACIDS

HALOGEN-SUBSTITUTED ACIDS

18.1. Isomerism. Methods of Preparation. Chemical Properties. Halogen-substituted acids include compounds which simultaneously contain a *halogen atom and a carboxyl group*. Both functions can be represented in a molecule once or several times.

It should be taken into account that *three types of structural isomerism* may be exhibited in halogen-substituted acids, like in other poly- and heterofunctional compounds. Besides the isomerism of the carbon skeleton and position isomerism, the *isomerism of the mutual position* of functional groups also appears in them. This makes it possible for a large number of isomers to exist. For example, there are two acids of the $C_4H_8O_2$ composition, i.e., butyric and isobutyric acids, while the number of isomers increases to five in the case of chlorosubstituted acids, $C_4H_7O_2Cl$.

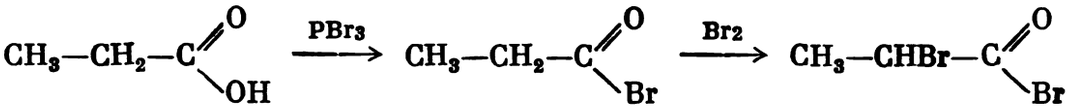
Halogen-substituted acids can be obtained by the most diverse methods: either by introducing a carboxyl group into a halogen-containing compound or, conversely, by introducing a halogen into carboxylic acid. The following two methods are of the greatest importance in introducing a halogen.

1. The substitution of a halogen for hydrogen in aliphatic acids, e.g., hydrogen atoms of the CH_3 group are gradually replaced by chlorine when acetic acid is being chlorinated:

$$\underset{\text{Acetic acid}}{CH_3—COOH} \xrightarrow{Cl_2} \underset{\text{Monochloroacetic acid}}{ClCH_2—COOH} \xrightarrow{Cl_2} \underset{\text{Dichloroacetic acid}}{Cl_2CH—COOH} \xrightarrow{Cl_2} \longrightarrow \underset{\text{Trichloroacetic acid}}{CCl_3—COOH}$$

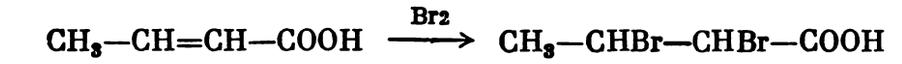
But free acids undergo halogenation with difficulty. Similar reactions occur far more readily with acid derivatives, such as esters and acid halides. A convenient variant of this reaction is bromination of acids by Hell-Volhard-Zelinsky method. Acid is acted on by bromine in the presence of phosphorus tribromide; this results in the formation of acid bromide, which is then subjected to bromi-

nation:

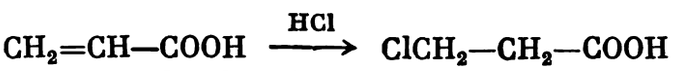


In these reactions, the halogen enters into the α-position towards the carboxyl.

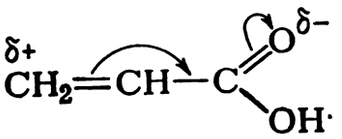
2. Addition of halogens or hydrogen halides to unsaturated acids. Dihalogen-substituted acids are obtained in the first case, and monohalogen-substituted ones, in the second case:



A hydrogen halide is added to acrylic acid and its analogues *contrary to Markovnikov's rule*:

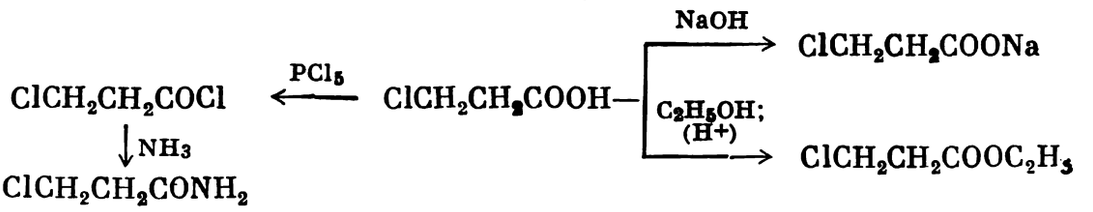


This occurs because the double bond is polarized under the action of the carboxyl group:

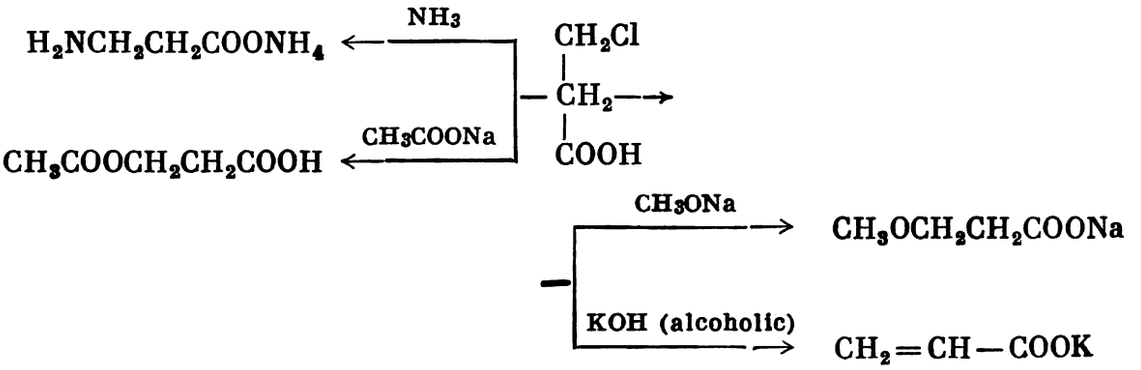


Halogen atoms and the carboxyl group in halogen-substituted acids possess mainly ordinary properties which are characteristic of these functions. For instance, a halogen is capable of undergoing nucleophilic substitution reactions (see Sec. 9.4), while a carboxyl group exhibits acidic properties and also yields functional derivatives which are common for acids.

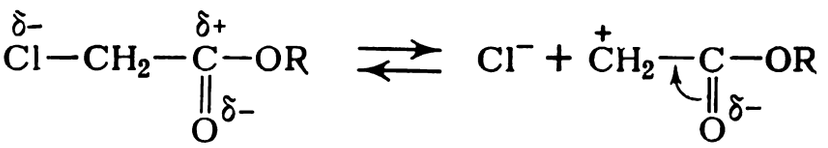
Reactions at the carboxyl group:



Reactions of a halogen:

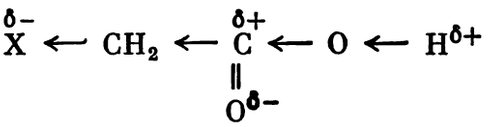


At the same time, both functional groups exert definite mutual effect, which is especially strong when they are close to one another. For instance, in α-halogen-substituted acid esters, halogen atoms are highly mobile, i.e., their reactivity increases under the influence of the carboxyl. This occurs because the joint action of a halogen and the C=O group, which withdraw electrons, creates a considerably high positive charge on the carbon atom that is between them, thus facilitating the attack of a nucleophilic reagent.



In more remote positions (β, γ, etc.), the mutual effect of the groups weakens.

In turn, a halogen, while drawing away electrons, affects the carboxyl group, as a result of which the acidic properties of the carboxyl increase. This is an exhibition of the negative inductive effect of a halogen (—*I* effect):



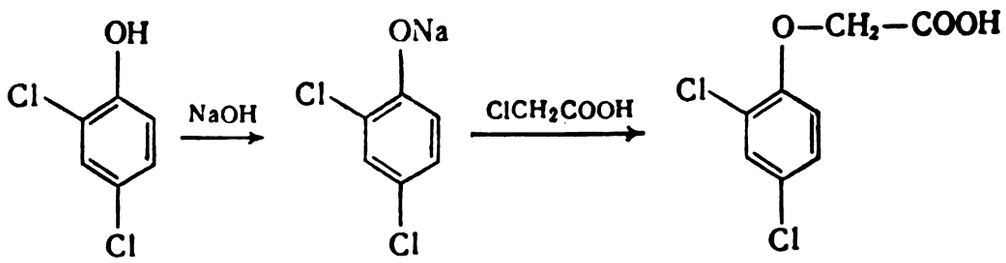
The strength of the inductive effect can be quantitatively estimated by the dissociation constant of a corresponding acid. The inductive effect increases as a transition is made from iodine to fluorine and as the number of halogen atoms grows, and it rapidly decreases as the distance between a halogen and a carboxyl widens. These regularities can be seen from a comparison of the following dissociation constants of acids:

	$K_a \times 10^{-5}$		$K_a \times 10^{-5}$
Acetic	1.76	Dichloroacetic	3320
Iodoacetic	75	Trichloroacetic	20,000
Bromoacetic	138	β-Chloropropionic	8.5
Chloroacetic	140	α-Chloropropionic	140

Other substituents, which possess the inductive effect and are capable of causing bond polarization, also affect the carboxyl.

Among halogen acids, *chloroacetic acid* is of the greatest practical importance. It is obtained in large amounts by chlorinating acetic acid and is used in organic synthesis, especially in obtaining indigo, and also *herbicides*, which are substances used in "chemically weeding" the fields, i.e., they are used for destroying weeds. A commonly used herbicide, 2,4-*dichlorophenoxyacetic acid*, is obtained from

dichlorophenol and chloroacetic acid:



HYDROXY ACIDS

18.2. Preparation Methods. Physical and Chemical Properties. *Hydroxy acids* are organic substances whose molecule has two functions: *the hydroxyl and the carboxyl functions*. The opportunities for isomerism in these compounds are perfectly the same as those in halogen acids.

Hydroxy acids can be *monobasic*, *dibasic*, and so forth, depending on the number of carboxyl groups, and they can be *dihydric*, *trihydric*, and so forth, depending on the number of hydroxyl groups (the hydroxyl in the carboxyl composition is also taken into account). Thus, the simplest hydroxy acid, *glycolic acid*, $HO—CH_2—COOH$, is a monobasic dihydric acid.

The hydroxyl group in the molecules of hydroxy acids can be at different distances away from the carboxyl group, and hence a distinction is made between α-, β-, γ- and other hydroxy acids:

$$\overset{\gamma}{C}—\overset{\beta}{C}—\overset{\alpha}{C}—COOH$$

There are very diverse methods of obtaining hydroxy acids, and some of the most important ones are given below:

1. Hydrolysis of halogen acids, e.g.,

$$ClCH_2COOH \xrightarrow{H_2O(H^+ \text{ or } HO^-)} \underset{\substack{\text{Glycolic}\\ \text{acid}}}{HO—CH_2—COOH}$$

2. Obtaining them from aldehydes and ketones through cyanohydrins (*cyanohydrin synthesis*):

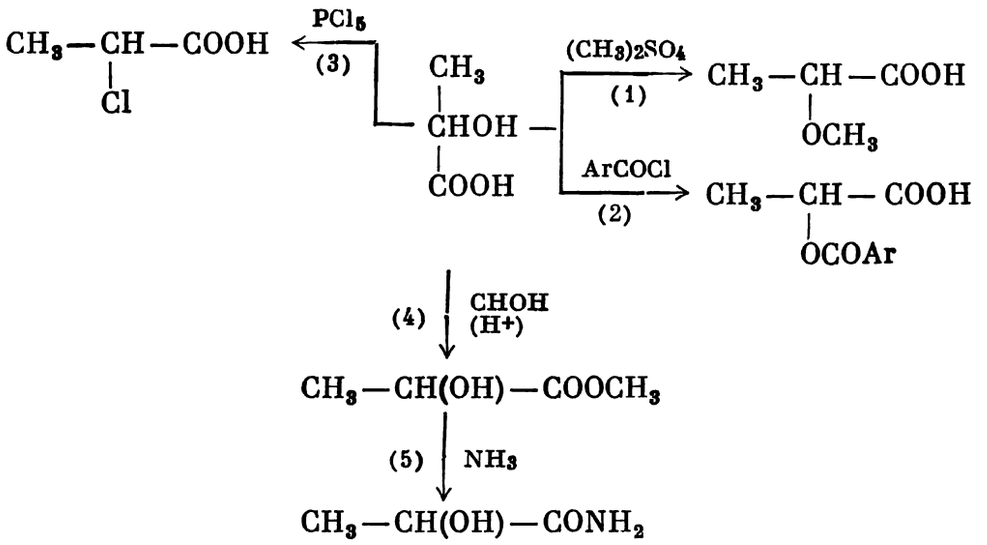
$$CH_3—CHO \xrightarrow{HCN} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CN \xrightarrow{H_2O} \underset{\substack{\text{Lactic acid}\\ (\alpha\text{-hydroxypropionic acid})}}{CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—COOH}$$

The first method is suitable for obtaining hydroxy acids with any mutual arrangement of functions, and the second one, for obtaining only α-hydroxy acids.

Hydroxy acids are, by their physical properties, high-boiling liquids or crystalline substances. They are, as a rule, well soluble

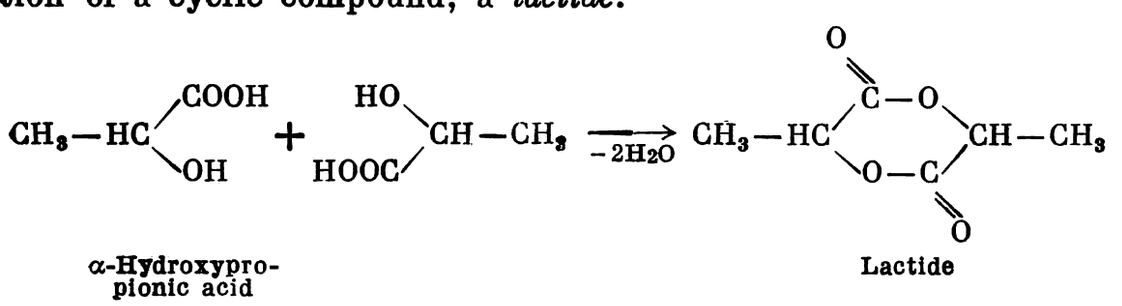
in water and poorly soluble in low-polar organic solvents (ether, benzene). This often hinders the separation of hydroxy acids from inorganic by-products, which are formed in the course of syntheses.

Like in other heterofunctional compounds, both functions generally retain their ordinary properties. For example, the *hydroxyl group* can be subject to alkylation (reaction 1, ether formation) and acylation (reaction 2, ester formation), and can be replaced by a halogen (reaction 3, halogen-substituted acids are obtained). The *carboxyl group* is capable of forming salts, esters (reaction 4), anhydrides, acid halides, amides (reaction 5) and other functional derivatives. Some of these reactions are illustrated by a scheme of transformations of lactic acid:



At the same time, there is new in the properties of hydroxy acids as compared with those of alcohols and acids: it is the reactions in which the hydroxyl and the carboxyl participate *simultaneously*. One of the most characteristic reactions of such a type occurs when hydroxy acids are heated, and transformation takes place differently, depending on the mutual arrangement of the hydroxyl and the carboxyl.

Water is eliminated when α-hydroxy acids, R—CHOH—COOH, are heated, and two acid molecules participate in the reaction. For example, lactic (α-hydroxypropionic) acid reacts with the formation of a cyclic compound, a *lactide*:



α-Hydroxypropionic acid

Lactide

Lactides are, by their structure, cyclic esters in whose formation each molecule of α-hydroxy acid reacts both as an acid and as an alcohol.

Beta hydroxy acids, R—CHOH—CH_2—COOH, readily lose water when they are heated, passing into unsaturated acids:

$$HOCH_2-CH_2-COOH \xrightarrow[-H_2O]{} CH_2=CH-COOH$$

β-Hydroxypropionic acid — Acrylic acid

When γ-hydroxy acids are heated, water is eliminated and internal esters known as *lactones* are formed:

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-COOH \xrightarrow[-H_2O]{} CH_3-CH\!<\!\begin{matrix}CH_2\\ O-C=O\end{matrix}$$

γ-Hydroxyvaleric acid — γ-Valerolactone

18.3. Optical Isomerism. Many hydroxy acids contain an *asymmetrical carbon atom*, which is attached to four *different substituents.* A tetrahedron, at whose vertices different substituents are found, has no element of symmetry. As a result, two incompatible spatial

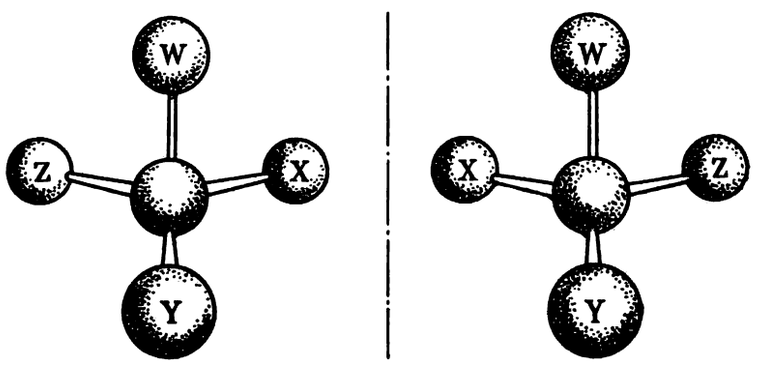


Fig. 18.1. Models of antipode (mirror) tetrahedrons

forms exist. They differ from one another like an unsymmetrical object does from its mirror image (Fig. 18.1). Substances having an asymmetrical carbon atom exist as two stereoisomers, and are known as *mirror* or *optical* isomers. They are given the second name, because the only difference between them in this case is their behaviour to polarized light. One mirror isomer rotates the plane of polarized light to the left, while another rotates it exactly by the same angle to the right. Therefore, a pair of mirror isomers is also called *optical antipodes.* All the other physical properties of optical antipodes are *the same.*

The ability of substances to rotate the plane of polarization is called *optical activity*. To measure it, use is made of a polarimeter, whose arrangement is schematically illustrated in Fig. 18.2.

Light source *1* passes through a polarization device *2* (a Nicol prism or a polaroid). In this case, it becomes plane-polarized. If analyzer *4* (second Nicol prism or a polaroid) is put in the path of polarized light, the strength of the light which gets into the observer's eye will depend on the mutual orientation of the prisms, i.e., on

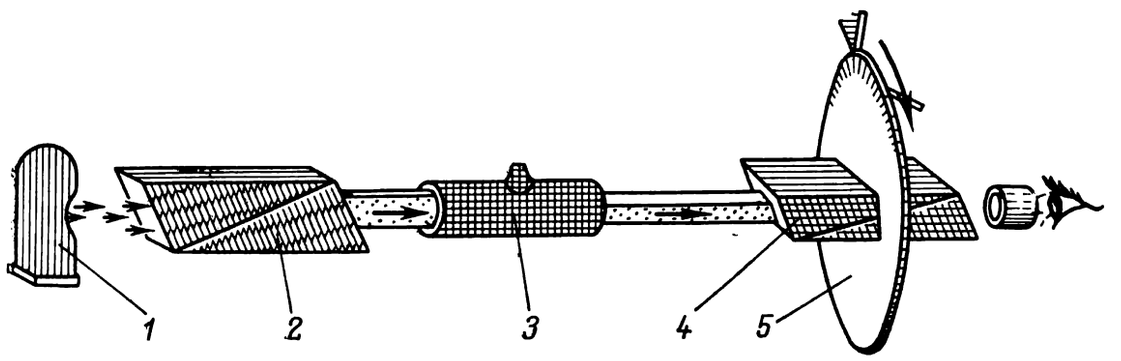


Fig. 18.2. A schematic description of a polarimeter:
1—light source; *2*—polarizer device; *3*—sample tube; *4*—analyzer; *5*—scale]

polarizer *2* and analyser *4*. Light passes without weakening when the orientation of the polarizing planes of both prisms ("parallel Nicols") is the same, while it is completely extinguished when Nicols are "crossed". If tube *3* having an optically active substance is put into the polarimeter which is set at complete extinction, the plane of polarized light will change and complete extinction will no longer occur. To extinguish again the ray which passes through the device, analyzer *4* must be turned to an angle which corresponds to the rotation of a substance in the tube. This angle is shown on the scale *5*. Observed rotation α depends on the nature of a substance, the layer length l and, for solutions, on concentration. Measured rotation is converted into *specific rotation*, i.e., the rotation of the plane of polarized light (in degrees) of one gram of a substance contained in one millilitre of a solution when the layer length is one decimetre (10 cm). The following formula is used for calculation:

$$[\alpha]=\frac{\alpha V}{pl}$$

where $[\alpha]$ = specific rotation;
α = observed rotation;
V = solution volume, ml;
p = amount of the solute, g;
l = length of the polarimetric tube, dm.

Specific rotation is a calculated quantity, and therefore one should not be surprised when its value is sometimes higher than 360°. It depends on the wavelength; in most cases it is determined for the yellow line of sodium and is then denoted by $[\alpha]_D$.

One of the simplest optically active substances, lactic acid, $CH_3—\overset{*}{C}HOH—COOH$, exists in three forms: the *dextrorotatory* form, which is denoted by the sign (+)- in front of the formula, the *levorotatory* form, denoted by the sign (—)-, and the *optically inactive* form, by the sign (±)-.

(+)-*Lactic acid* has $[\alpha]_D^{15}$ + 3.82° (10 per cent aqueous solution). It is a crystalline substance which melts at 25-26°C. It is this dex-

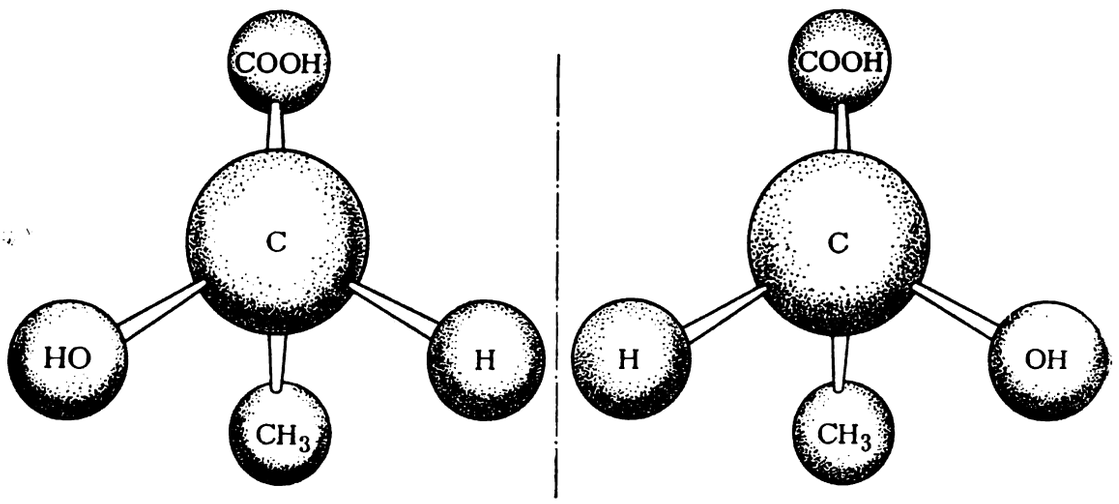


Fig. 18.3. Optical antipodes of lactic acid

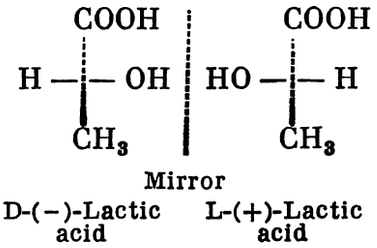
trorotatory form which is found in muscle tissue, and therefore it has become known as *sarcolactic* acid.

Levorotatory (—)-lactic acid cannot be distinguished from the dextrorotatory form by its properties, except for the sign of rotation $[\alpha]_D^{15}$ — 3.82°.

Optically inactive (±)-*lactic acid*, the so-called *fermentation lactic acid*, is a crystalline substance which melts at 18°C. It is very difficult to obtain this acid in a solid state, and it usually exists as dense syrup which mixes with water in all proportions. Investigations have shown that fermentation lactic acid has no optical rotation, because it is a mixture of equal parts of both (+)- and (—)-lactic acid. Such mixtures are called *racemates*.

The existence of a pair of optical antipodes is an exhibition of mirror isomerism of lactic acid (Fig. 18.3). The structure of optical antipodes of lactic acid is represented in the following way with

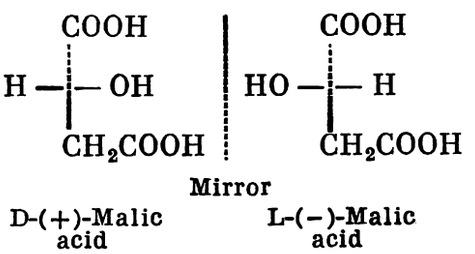
the aid of the *Fischer projection formulas*:



In these formulas, the substituents at the top and bottom (COOH, CH_3) are imagined as lying *behind the plane* of the paper, and the substituents attached on the wings (left and right) (H, OH), *in front of the plane* of the paper. An asymmetric carbon atom lying on the paper plane, though not represented in the projection formula, is in the centre of the formula at the point of intersection of both lines. Optical antipodes are not superimposable, and they differ from one another like the right hand does from the left one, and like an object does from its mirror image.

The letters D- and L- in the names of hydroxy acids indicate their *configuration*, i.e., the spatial arrangement of substituents around an asymmetric carbon atom. The letter D- stands for hydroxy acids whose hydroxyl group in a Fischer projection formula is on the right; the notation L- is used if the hydroxyl group in the projection formula stands on the left.

Optical isomerism is observed also for malic acid, HOOC—$\overset{*}{C}$HOH—CH_2—COOH.



(—)-Malic acid is found naturally.

The molecule of *tartaric acid*, HOOC—$\overset{*}{C}$HOH—$\overset{*}{C}$HOH—COOH, has two like asymmetric atoms, and each of them can exist in a configuration which creates either levorotation (I) or dextrorotation (II). The following combinations are possible:

(—)- (—)-	(+)- (+)-	(—)- (+)-
I	II	III
Levorotatory	Dextrorotatory	Mesotartaric

An equimolecular mixture of forms I and II gives racemic tartaric acid, which is also called *racemic acid*; mesotartaric acid (form III) is optically inactive owing to the intramolecular compensation of the rotation of asymmetric centres.

Forms I and II are a pair of optical antipodes; all their physical properties are the same, except for the sign of optical rotation. These forms are *diastereomers* of mesotartaric acid. That is the name of a group of stereoisomers with two or more asymmetric centres that are not mirror images of each other; they have the same configuration at one asymmetric atom at least and, at the same time, different configurations at one asymmetric atom at least. The main distinguishing feature of diastereomers is that their physical properties *differ* in every pair.

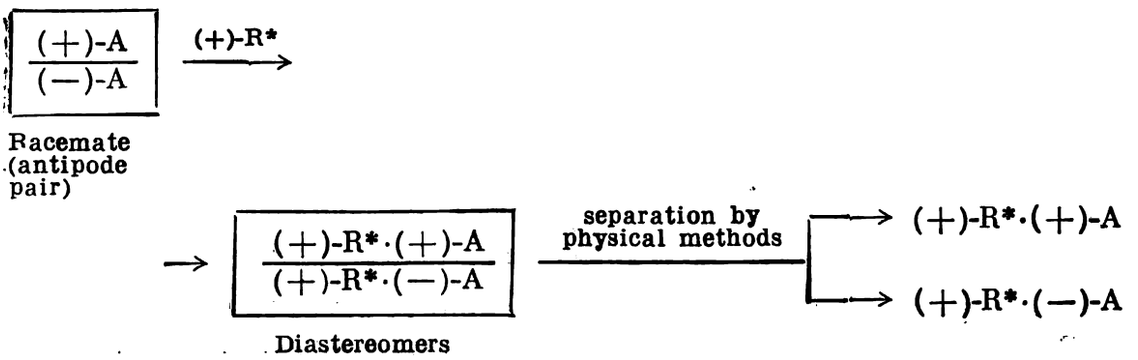
(+)-Tartaric acid is widely distributed naturally. Its levorotatory antipode was first isolated in 1848 by Pasteur in his classical investigations, which became the basis of the stereochemistry of optically active substances.

In carefully studying the kinds of crystals of the sodium ammonium salt of racemic (optically inactive tartaric) acid, Pasteur noticed crystals of two mirror forms (which differ from one another like an unsymmetric object does from its mirror image). After separating these crystals and dissolving them individually in water, he obtained optically active solutions: dextrorotatory and levorotatory. This experiment was the first example of *resolution of a racemate into optical antipodes*, i.e., separating the levorotatory antipode from the dextrorotatory one.

Pasteur later worked out two more methods of dividing racemates by taking tartaric acid as an example.

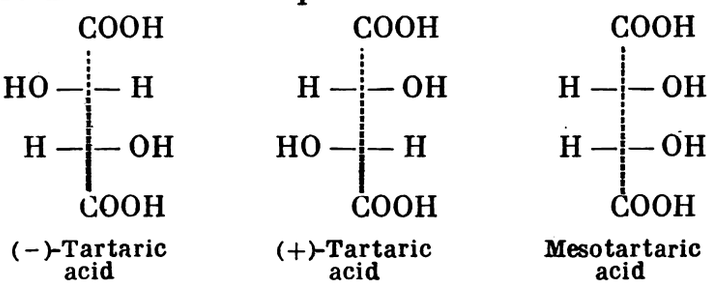
The *biochemical* method, which is based on the fact that microorganisms (e.g., mould bacteria, *penicillum glaucum*) consume only one antipode from a racemate for their vital activity; the second antipode remains untouched and can be separated;

the *chemical* method, which is based on the conversion of an optical antipode pair (i.e., a racemate) into a *diastereomer* pair. To this end, a racemate is allowed to react with a suitable optically active reagent. Since diastereomers differ in physical and chemical properties, they can be separated more or less readily. The entire process can be schematically illustrated as follows:

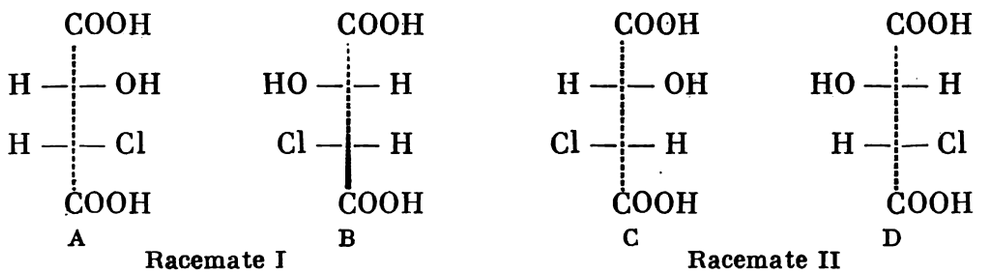


where (+)-R* is an optically active reagent which is eliminated after diastereomers are separated.

Tartaric acid is also the first optically active substance for which *absolute configuration* was determined by a special X-ray method in the 1950's, i.e., conformity was established between the sign of optical rotation and the spatial model, and, consequently, the projection formula which expresses this model:



A more complicated case of stereoisomerism is when a compound has two *different* asymmetric atoms. An example is *chloromalic acid*, which exists, like all similar compounds, in four optically active forms that constitute two racemates:



Stereoisomers, whose configurations are described by formulas A, B and C, D, are antipode pairs, accordingly. Any other combination (A and C, A and D, B and C, B and D) forms a pair of *diastereomers*. In general, a molecule which has n different asymmetric atoms exists as 2^n individual spatial forms (racemates are not taken into account).

18.4. Important Individual Hydroxy Acids. Hydroxy acids include compounds which are important in living nature and are also used industrially.

Lactic acid is so called, because it is formed in sour milk. The source of lactic acid is lactose, which undergoes fermentation under the action of special microorganisms, i.e., *lactobacilli*.

Other saccharides can also be subjected to lactic fermentation. Such processes occur in the preparation of cheese and sour cabbage, and in fodder ensilage:

$$C_6H_{12}O_6 \longrightarrow 2CH_3—CHOH—COOH$$

Until recently, lactic acid was obtained industrially only by lactic fermentation. At present, it is industrially synthesized from acetaldehyde:

$$CH_3—\underset{\underset{O}{\|}}{C}—H \xrightarrow{HCN} CH_3—\underset{\underset{OH}{|}}{CH}—CN \xrightarrow{H_2O} CH_3—\underset{\underset{OH}{|}}{CH}—COOH$$

Lactic acid is used as a preservative in the food industry, in leather tanning and in textile finishing, and as an initial substance in many syntheses.

(—)-*Malic acid* is often found in various acid fruits: apples, grapes and mountain ash. It is a crystalline substance which melts at 100°C and dissolves readily in water.

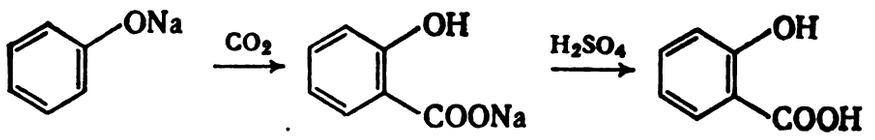
(+)-*Tartaric acid* is a crystalline substance found in many plants, especially grapes and mountain ash. The acid potassium salt of tartaric acid is sparingly water-soluble (it precipitates as tartar in wine casks). Its formation is used in analysis for detecting potassium. When tartar is neutralized by caustic soda, a mixed potassium sodium salt of tartaric acid, known as *Seignette salt*, is formed.

Citric (2-*hydroxy*-1,2,3-*propanetricarboxylic*) *acid*

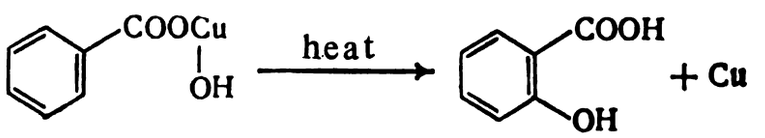
$$HOOC-CH_2-\underset{\displaystyle COOH}{\overset{\displaystyle |}{C}}OH-CH_2-COOH$$

is a crystalline substance which melts at 153°C and readily dissolves in water. It is found in the fruits of citrus plants (lemons, oranges), grapes, gooseberries, raspberries and beet. Citric acid is contained as a salt with nicotine in tobacco. It is used in dyeing, medicine, and in confectionery and food industries.

Salicylic (*o-hydroxybenzoic*) *acid* is the most important hydroxy acid of the aromatic series. It is obtained industrially by the Kolbe-Schmitt reaction as carbon dioxide acts on sodium phenoxide (125°C; 4-7 kg/cm^2); the yield is almost quantitative:

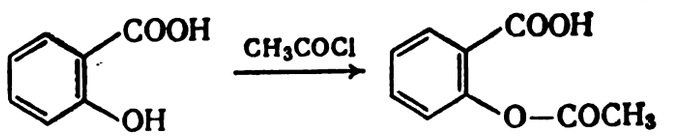


In a more modern method, use is made of benzoic acid that is transformed into a basic copper salt from which salicylic acid is formed on heating:



Salicylic acid is a colourless crystalline substance which melts at 159°C, it dissolves sparingly in water, but well in alcohol. It is used in analysis for the colorimetric determination of iron (violet colouring) and copper (green colouring), and also as a fluorescent indicator. Since salicylic acid acts as an antiseptic, it is used in tinning fruits and vegetables.

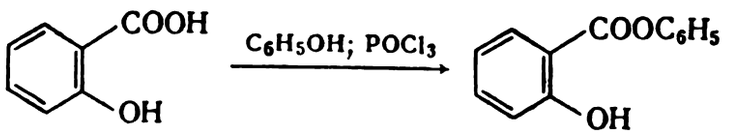
Many derivatives of salicylic acid are used as medicinals. The one known best of all is *acetylsalicylic acid* (*aspirin*). It is obtained when acetic anhydride or acetyl chloride acts on salicylic acid, causing the acylation of the phenol hydroxyl:



Aspirin

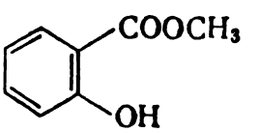
Aspirin is a febrifuge and an analgesic. It was discovered in the nineteenth century, but so far it has lost none of its importance.

Another medicinal, *salol*, is used against gastroenteritic diseases, and it is an ester of salicylic acid and phenol:



Salol

Methyl salicylate, a product of interaction between the carboxyl group of salicylic acid and methyl alcohol, is used externally in various ointments. It is represented as:



POLYHYDROXYBENZOIC ACIDS. TANNING AGENTS

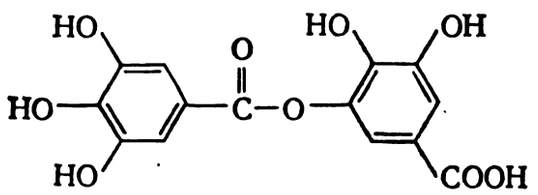
18.5. Individual Acids. *Gallic acid* is 3,4,5-trihydroxybenzoic acid. It is found naturally as a component of gallnuts (see further), oak bark, tea leaves and many other plants from which Scheele first obtained it as early as the end of the eighteenth century. It is a crystalline substance which melts at 293°C; it dissolves sparingly in cold water, and readily in hot water. It oxidizes and darkens in the air. When it is heated, it readily loses carbon dioxide and turns into pyrogallol (see Sec. 10.10).

Other phenolic acids, whose carboxyl group is in the *ortho-* or *para-*position towards the hydroxyl, are also comparatively readily decarboxylated (this is true of salicylic acid as well).

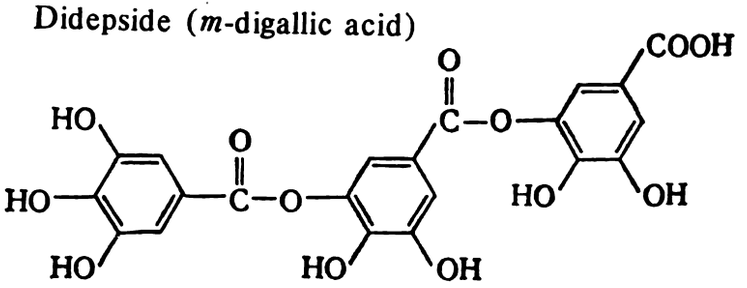
Tanning agents. When leather is being dressed, hides are subjected to *tanning*, in the course of which hide strength increases, swelling

under the action of water decreases, and the required elasticity is acquired. Substances which cause tanning are known as tanning agents. The main source of tanning agents was once the oak bark. At present, inorganic substances [salts of Cr(III), Al, etc.] and organic substances of plant or synthetic origin are used for tanning.

Among the most important tanning agents are *tannins*, which are extracted from pathological growths on oak leaves (gallnuts*). There are several types of tannins. Many of them are esters composed from several molecules of gallic acid, and are known as *depsides*:



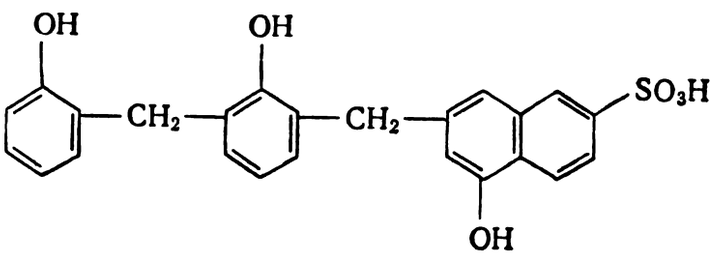
Didepside (*m*-digallic acid)



Tridepside

Other tannins are esters of gallic acid with carbohydrates, in most cases with glucose (glucosides, see Sec. 19.3).

Chemically, synthetic tanning agents are sulpho-derivatives of polyhydric phenols, e.g.,

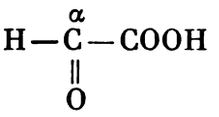


ALDEHYDO AND KETO ACIDS

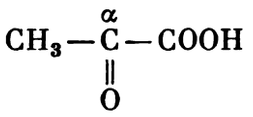
18.6. Nomenclature. Isomerism. General Methods of Preparation. Aldehydo and keto acids are heterofunctional compounds whose molecule contains simultaneously the carbonyl (aldehyde or keto)

* Ink was formerly made from gallnuts by mixing tannin with ferrous salts. Such a solution is almost colourless. Oxidation of the iron-tannin compound produces a stable blue-black colour.

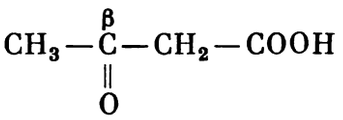
group and the carboxyl group. The names of aldehydo and keto acids are composed on the basis of the corresponding carboxylic acids with an indication of the position of the carbonyl group. Trivial names of acids are often used:



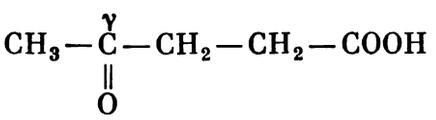
Glyoxylic acid



Pyroracemic acid (2-oxopropanoic acid)



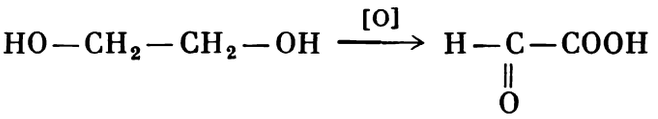
Acetoacetic acid (3-oxobutyric acid)



4-Oxovaleric acid

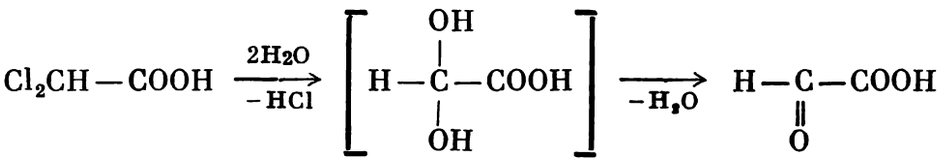
To obtain aldehydo and keto acids, use can be made of many reactions by means of which either the carbonyl group is introduced into a carboxyl compound or, conversely, the carboxyl is introduced into a compound which already contains the aldehyde or the keto group. Such methods are:

1. Glycol oxidation:



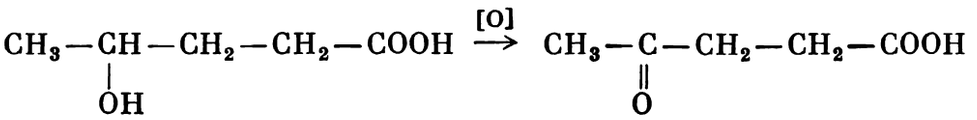
Ethylene glycol — Glyoxylic acid

2. Hydrolysis of dihalogenated acids:



Dichloroacetic acid — Glyoxylic acid

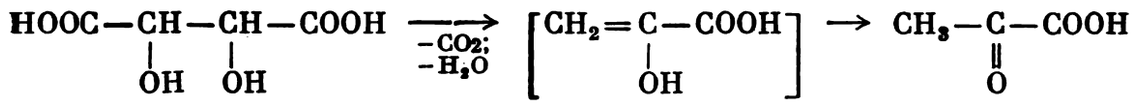
3. Hydroxy acid oxidation:



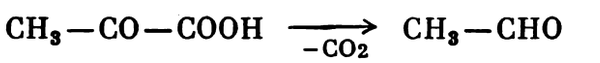
γ-Hydroxyvaleric acid — 4-Oxovaleric acid

18.7. Individual Keto Acids. Alpha-oxopropanoic acid is the simplest of them by its structure, and it is usually called *pyroracemic acid* or *pyruvic acid*. The term reflects the method of obtaining it, i.e., by heating racemic (tartaric) acid (from the Greek word "pyros", meaning "fire"). In the course of this reaction, the molecule of tartaric

acid loses carbon dioxide and water:

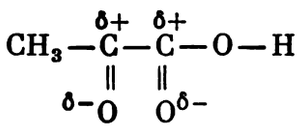


Pyroracemic acid is a liquid with a peculiar odour. When it is heated further, it loses another molecule of carbon dioxide and turns into acetaldehyde:



Such a decarboxylation reaction which occurs on heating is characteristic of other α-keto acids.

The carboxyl group of pyruvic acid exhibits its characteristic properties, and we know salts, esters, amides and other carboxyl-derivatives of pyruvic acid. In turn, the keto group enters into reactions which are characteristic of it: it forms oxime, hydrazone and phenylhydrazone, and adds sodium bisulphite and hydrocyanic acid. All the reactions of the carbonyl group occur more readily for pyruvic acid than for ordinary ketones due to the intensification of the positive charge on carbonyl carbon under the influence of the carboxyl group:



In turn, the carbonyl group affects the carboxyl group, thus increasing its acidity: therefore, pyroracemic acid is almost 500 times stronger than propionic acid.

The structurally simplest keto acid is *acetoacetic acid*, $CH_3—CO—CH_2—COOH$. Like all other β-keto acids, it is unstable in the free state and decomposes with the loss of carbon dioxide:

Salts, esters and other functional derivatives of acetoacetic acid are quite stable. Among the derivatives of acetoacetic acid, its ethyl ester is of special importance, and it is usually called *acetoacetic ester*. It is obtained, like other β-keto esters, in *ester condensation*.

18.8. Claisen Condensation. Claisen condensation is an interaction of two molecules of an ester with the formation of β-keto ester. This reaction occurs under the action of basic catalysts. Its simplest and at the same time most important example is the condensation of two molecules of ethyl acetate with the formation of ethyl

acetoacetate:

$$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5+CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{Na} \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5+C_2H_5OH$$

Alkoxides, sodamide and sodium hydride, besides metallic sodium, can serve as condensating agents.

The mechanism of this reaction is similar to aldol condensation, which we have considered earlier (see p. 226). A proton is eliminated from the CH_3 group of ethyl acetate under the action of a strong base (sodium ethoxide), and the *carbanion* is formed:

$$CH_3COOC_2H_5+C_2H_5O^- \rightleftarrows :\bar{C}H_2COOC_2H_5+C_2H_5OH$$

This carbanion then acts as a methylene component, being added to another molecule of ethyl acetate that is a carbonyl component:

$$CH_3-\overset{\delta+}{\underset{\underset{O^{\delta-}}{\|}}{C}}-OC_2H_5+:\bar{C}H_2-COOC_2H_5 \rightarrow CH_3-\underset{\underset{O^-}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}-CH_2-COOC_2H_5$$

A new anion is formed after the alcohol molecule is eliminated, and it turns into acetoacetic ester as the reaction mixture is decomposed by dilute acid:

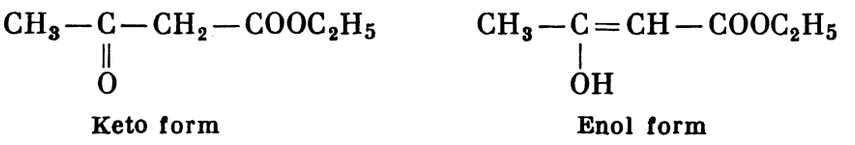
$$CH_3-\underset{\underset{O^-}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}-CH_2-COOC_2H_5 \xrightarrow[-C_2H_5OH]{} CH_3-\underset{\underset{O^-}{|}}{C}=CH-COOC_2H_5 \xrightarrow{H^+} \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5$$

Like ethyl acetate, other esters having the general formula of RCH_2COOR' also undergo ester condensation. Esters of the type of $R_2CHCOOR'$ are incapable of undergoing condensation under the action of sodium, and the reaction occurs only when use is made of stronger condensating agents, such as triphenylmethylsodium $(C_6H_5)_3CNa$:

$$2(CH_3)_2CH-COOC_2H_5 \xrightarrow{(C_6H_5)_3CNa} (CH_3)_2CH-\underset{\underset{O}{\|}}{C}-\underset{\underset{COOC_2H_5}{|}}{C}(CH_3)_2$$

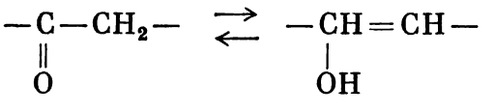
18.9. Tautomerism of Acetoacetic Ester. Acetoacetic ester was the first organic compound which served as an example in the discovery

and thorough study of *tautomerism*, i.e., the coexistence of isomeric forms which are in equilibrium and are capable of being readily interconverted (dynamic isomerism). For ethyl acetoacetate, the following structures are concerned:



Keto form Enol form

The interconversion of both forms consists in the migration of the double bond (i.e., mobile π-electrons) and hydrogen:



Such a type of tautomerism is called *keto-enol tautomerism*. It is a particular case of tautomerism involving hydrogen migration, and is known as *prototropy*. In this case, hydrogen becomes mobile under the action of the CO and COOR groups.

The conclusion that keto and enol forms of acetoacetic ester exist was first drawn when the chemical properties of this compound were being studied (see further); later, both forms were separated in individual states. If ordinary ethyl acetoacetate (it contains ca. 93 per cent of the keto form and ca. 7 per cent of the enol form) is dissolved in petroleum ether and greatly cooled, e.g., down to —78°C by dry ice in acetone, the keto form will be isolated as crystals which melt at —39°C (the density of the pure keto form d_4^{10} is 1.0368, and the refractive index n_D^{10}, 1.4425). It gradually turns into an equilibrium mixture of keto and enol forms. Pure enol form can be obtained most simply by distilling acetoacetic ester, i.e., the enol form boils at a lower temperature than the keto form, and its m.p. is —44°C, d_4^{10}, 1.0119, and n_D^{10}, 1.4480. When the enol form is allowed to stand, it also turns into an equilibrium mixture.

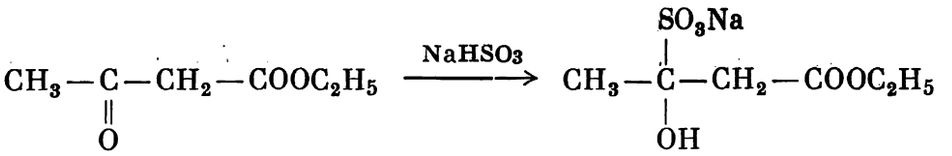
The interconversion of tautomeric forms of acetoacetic ester is accelerated by acid and alkalies. Even negligible traces of alkali, which get into the liquid from the glass of laboratory ware and from tobacco smoke, have a strong catalytic effect. The content of the keto and enol forms in solutions depends on the nature of the solvent and on temperature. For example, a solution of acetoacetic ester in water contains 0.4 per cent of the enol form; in methanol, the figure is 6.87 per cent, in benzene, 16.2 per cent, and in hexane, 46.4 per cent.

Ordinary acetoacetic ester produces reactions of both the keto and enol forms. Notwithstanding the low content of the enol form in equilibrium acetoacetic ester, the whole of acetoacetic ester can pass into a derivative of the enol form in the corresponding reactions

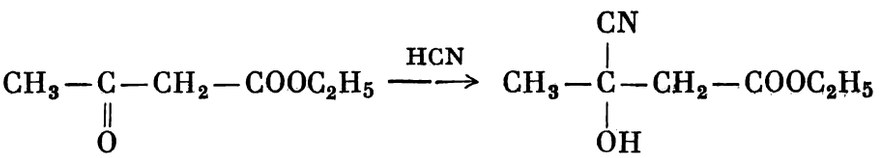
because, as this form is being spent, its reserve is replenished again as a result of the enolization of the keto form.

Reactions characteristic of the keto form:

(a) Addition of sodium bisulphite with the formation of a bisulphite derivative which is characteristic of carbonyl compounds:



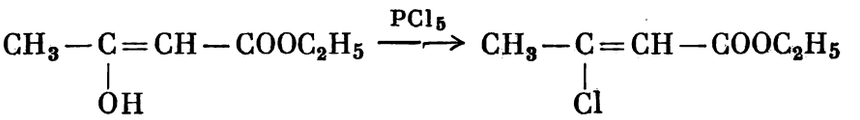
(b) Addition of hydrocyanic acid with the formation of cyanohydrin:



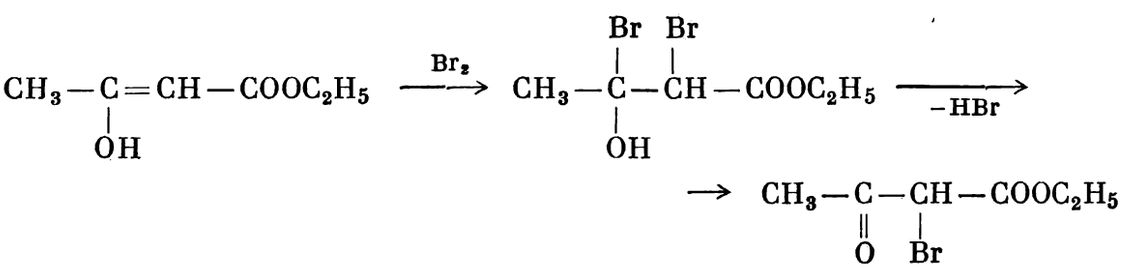
Reactions characteristic of the enol form:

(a) Red-violet colouring produced with the ferric chloride solution; in this case, complex iron chelates are formed.

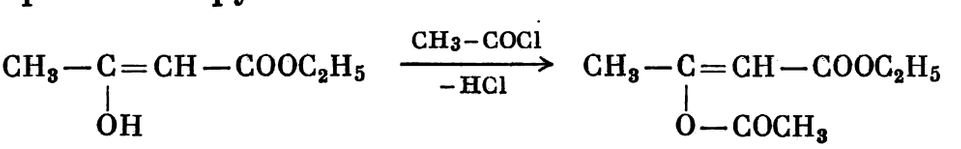
(b) Reaction with phosphorus pentachloride, resulting in the formation of β-chlorocrotonate:



(c) Rapid addition of bromine across the double bond in the cold. Dibromide which is initially formed readily eliminates hydrogen bromide and turns into a derivative of the *keto* form, i.e., α-bromoacetoacetic ester:



(d) Acylation at the OH group under the action of acetyl chloride in the presence of pyridine:



(e) Alkylation at the OH group by diazomethane:

$$CH_3-\underset{\displaystyle OH}{\underset{|}{C}}=CH-COOC_2H_5 \xrightarrow[-N_2]{CH_2N_2} CH_3-\underset{\displaystyle OCH_3}{\underset{|}{C}}=CH-COOC_2H_5$$

(f) Reactions with metallic sodium, sodium alkoxide or alkali, resulting in the formation of *sodium ethyl acetoacetate* (β-hydroxycrotonate alkoxide):

$$CH_3-\underset{\displaystyle OH}{\underset{|}{C}}=CH-COOC_2H_5 \xrightarrow[-C_2H_5OH]{C_2H_5ONa} CH_3-\underset{\displaystyle ONa}{\underset{|}{C}}=CH-COOC_2H_5$$

Sodium ethyl acetoacetate is of great importance in the synthesis of various organic compounds. Many syntheses are effected by treating it with alkylating and acylating agents. An interesting and important feature of these reactions is the *transfer of the reaction centre.*

The *alkylation* reaction occurs in the following way:

$$CH_3-\underset{\displaystyle ONa}{\underset{|}{C}}=CH-COOC_2H_5 \xrightarrow[-NaI]{CH_3I} CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOC_2H_5$$

In this reaction, the alkyl halide radical does not take the place of its predecessor, i.e., the sodium atom, which is linked with oxygen, but turns out to be at α-carbon.

The *acylation* of sodium ethyl acetoacetate occurs in the same way:

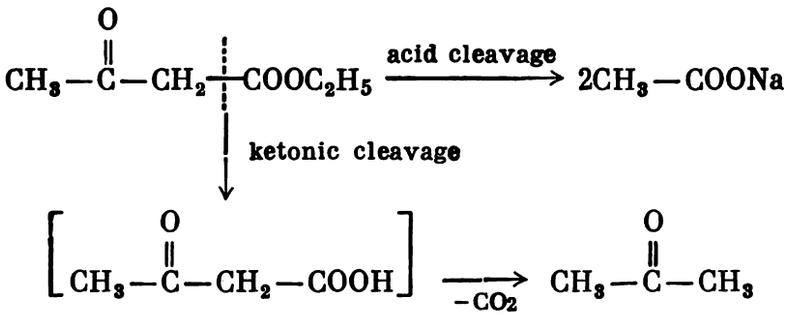
$$CH_3-\underset{\displaystyle ONa}{\underset{|}{C}}=CH-COOC_2H_5 \xrightarrow{C_6H_5COCl} CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle COC_6H_5}{\underset{|}{CH}}-COOC_2H_5$$

Iodine can be used to "crosslink" two molecules of ethyl acetoacetate, this reaction occurs in a similar way:

$$2CH_3-\underset{\displaystyle ONa}{\underset{|}{C}}=CH-COOC_2H_5 \xrightarrow[-2NaI]{I_2} \begin{matrix} O \\ \| \\ CH_3-C-CH-COOC_2H_5 \\ \qquad\qquad | \\ CH_3-C-CH-COOC_2H_5 \\ \| \\ O \end{matrix}$$

18.10. Synthesis with the Aid of Acetoacetic Ester. Derivatives of acetoacetic ester obtained by alkylation or acylation are interesting not in themselves, but as starting substances for further transformations. Reactions in which these compounds undergo ketonic and acid cleavage are of great importance. Let us begin our consideration

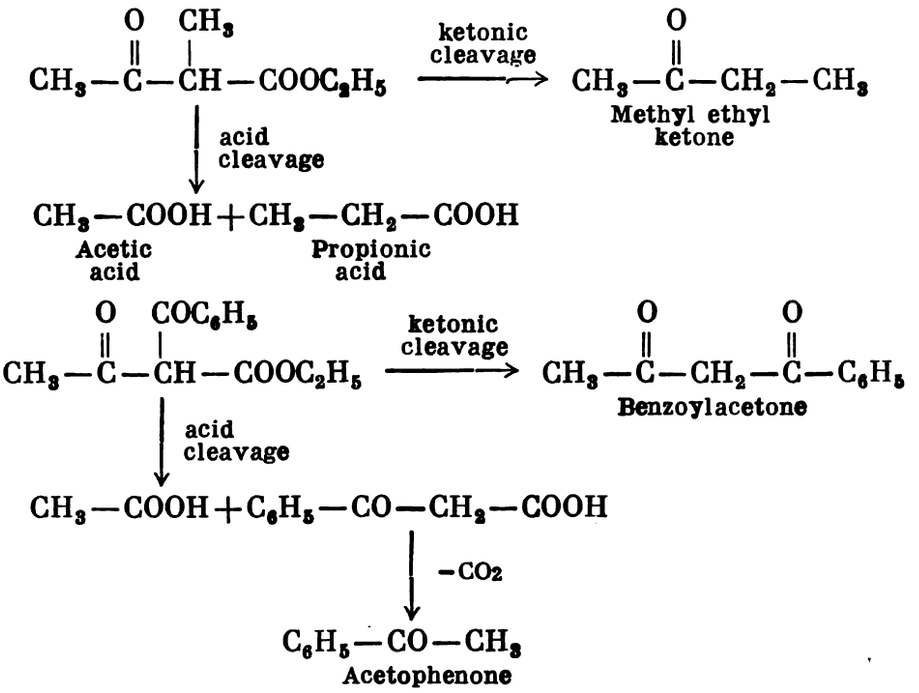
of them by taking the example of ethyl acetoacetate itself:

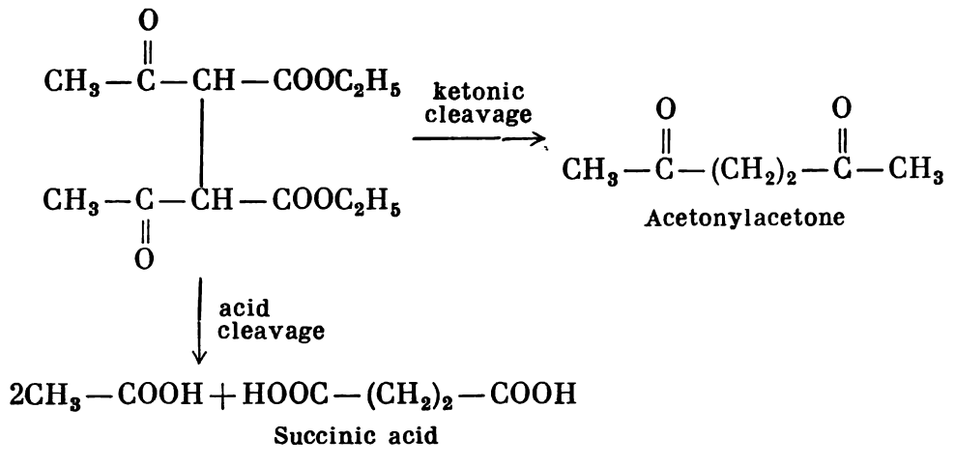


Acid cleavage, which occurs under the action of concentrated alcoholic alkali, formally consists in the rupture of the bond between α-carbon and the keto group and in simultaneous hydrolysis of the ester grouping. In this case, two molecules of acetic acid are formed (in the form of a salt). In fact, this process is more complicated, and therefore its mechanism will not be considered here.

The ester group is saponified, and free acetoacetic acid is isolated, under the action of weak alkalies or dilute mineral acids. Acetoacetic acid is unstable, like all β-keto acids: *ketonic cleavage* occurs, i.e., carbon dioxide is eliminated and ketone, being acetone in this case, is formed.

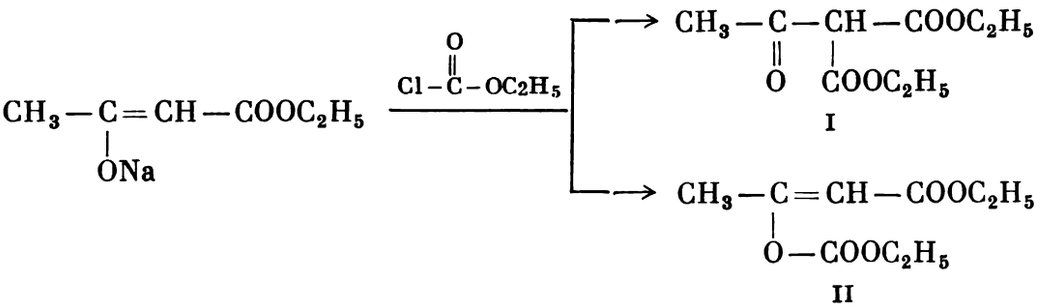
Substituted acetoacetic esters can be subject to ketonic and acid splitting quite similarly; in this case, ketones of greater complexity, homologues of acetic acid, diketones, dicarboxylic acids, and others can be obtained. For example, the following products are formed when ethyl acetoacetate derivatives described earlier (p. 378) are split:





Ethyl acetoacetate can be used to obtain practically any methyl ketones of the general formula $CH_3—CO—R$, homologues of acetic acid $RR'CH—COOH$, diketones, and dicarboxylic acids.

18.11. Tautomerism and Dual Reactivity. Let us return to the alkylation and acylation reactions of sodium ethyl acetoacetate. As we have already seen, the derivatives of the keto form (C-derivatives) are engendered in these reactions. But reactions which produce the derivatives of the enol form (O-derivatives) are also known. For example, both the C-derivative I and the O-derivative II are formed when chlorocarbonate (chloroformate) ester interacts with sodium ethyl acetoacetate:



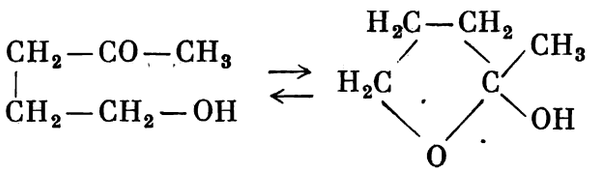
This begs the question: are C- and O-derivatives formed from the same substance (sodium ethyl acetoacetate, which has an enol structure), or could it be that the source of the O-derivative is the enolate of acetoacetic ester, which structurally corresponds to it, and the source of the C-derivative is a different tautomeric form of the sodium derivative, $CH_3—CO—CHNa—COOC_2H_5$? Could it be that sodium ethyl acetoacetate, like ethyl acetoacetate itself, is capable of undergoing tautomerism?

As for tautomeric compounds in general, the question can be formulated in the following way: are dual reactivity and tautomerism inseparable, or can the formation of two series of derivatives be observed also when tautomerism is absent? This is an open question even now.

Convincing evidence of dual reactivity without tautomerism (i.e., without the existence of two interconvertible isomeric forms) is given in A. N. Nesmeyanov's works. In practice, both phenomena are most frequently interconnected, and it is difficult to separate dual reactivity from tautomerism.

Keto-enol tautomerism can be detected also in several other substances besides ethyl acetoacetate, and both forms can differ in their stability. The structure of such substances can be generally expressed by the formula $X—CH_2—Y$, where X and Y are the groups RCO, COOR, CN and NO_2.

The equilibrium of the keto-enol forms and the dual reactivity of β-dicarbonyl compounds are merely an example of tautomerism commonly found in organic chemistry. For instance, tautomerism (or dual reactivity) is found in compounds containing the hydroxyl and carbonyl groups together, e.g.,



γ-Acetopropyl alcohol (carbonyl form) ⇄ α-Hydroxy-α-methyltetrahydrofuran (cyclic form)

This type of tautomerism is of the greatest importance in the carbohydrate series, and it will be discussed in greater detail later in the section on carbohydrates.

At present, tautomerism is regarded as dynamic isomerism, i.e., an equilibrium of readily interconvertible forms. A careful consideration will show that, in essence, there is no clearly-defined boundary between tautomerism and isomerism.

For instance, the keto and enol forms of ethyl acetoacetate, which are in tautomeric equilibrium at room temperature, become stable, separately existing isomers when they are cooled down to —70°C. For example, these compounds will be subject not to tautomerism, but to isomerism under the conditions of winter in the Antarctic.

On the other hand, propyl bromide and isopropyl bromide are stable, separately existing isomers under ordinary conditions, and tautomeric equilibrium is established between them when they are heated up to 250°C:

$$CH_3—CH_2—CH_2Br \underset{\longleftarrow}{\overset{250°C}{\longrightarrow}} CH_3—CHBr—CH_3$$

Chapter 19

CARBOHYDRATES

Carbohydrates are substances of the $C_nH_{2n}O_n$ composition; they are of paramount importance biochemically and are widespread naturally. They include various saccharides, starch, and cellulose. The term *carbohydrates* has been retained for them since the time when their structure was still unknown, but their composition had been ascertained; it corresponded to the general formula of $C_n(H_2O)_m$. According to this formula, carbohydrates were regarded as the hydrates of carbon, i.e., compounds of carbon and water, and hence the name "carbohydrates".

19.1. Classification. Physical Properties. Occurrence in Nature. The classes of carbohydrates are:

monosaccharides are compounds whose chemical nature is that of hydroxyaldehydes or hydroxyketones, but which exist mainly in tautomeric cyclic forms;

oligosaccharides (from the Greek word "oligos", meaning "few"), which are the products of condensation of several monosaccharide molecules with the loss of water (according to the ether type). The most important oligosaccharides are *disaccharides*, whose molecules are composed of two monosaccharide units;

polysaccharides, which are high-molecular-weight substances that are the products of condensation of a large number of monosaccharide molecules.

Monosaccharides are divided into *tetroses*, *pentoses*, *hexoses* and other groups, depending on the number of oxygen atoms which are in their composition (it is usually equal to the number of carbon atoms). Moreover, monosaccharides are divided into *aldoses* and *ketoses*, depending on whether the monosaccharide molecule has the aldehyde or keto group. Carbohydrate classification can be represented by the following scheme:

Monosaccharides	**Disaccharides $C_{12}H_{22}O_{11}$**
Tetroses $C_4H_8O_4$	saccharose (sucrose)
erythrose	lactose
threose	maltose
Pentoses $C_5H_{10}O_5$	cellobiose
arabinose	

	Polysaccharides
xylose	
ribose	$(C_5H_8O_4)_n$
Hexoses $C_6H_{12}O_6$	pentosans
glucose	$(C_6H_{10}O_5)_n$
mannose	cellulose
galactose	starch
fructose	glycogen

There is a great variety of monosaccharides, and the most widely distributed ones are aldopentoses and aldohexoses. In the scheme, all the monosaccharides except fructose are aldoses. The most widely distributed aldohexose is glucose.

Glucose is also called *grape sugar*, because it is contained in grape juice. Besides grapes, glucose is found in other sweet fruits and generally in different parts of plants. It is just as widespread in the animal kingdom: about 0.1 per cent of it is contained in blood. Glucose is carried by blood through the whole body and is the main source of energy for the organism. It is in the composition of the most important natural disaccharides (sucrose, maltose and lactose) and polysaccharides (cellulose and starch).

Another monosaccharide which is widely distributed in the vegetable kingdom is *fructose* (ketohexose), or *fruit sugar*. Fructose together with glucose is contained in sweet fruits, and it is in the composition of sucrose, a disaccharide, and inulin, a polysaccharide (fructose is usually obtained by hydrolyzing the latter). By extracting sweet juices from flowers, bees make honey, which, by its chemical composition, is mainly a mixture of glucose and fructose. This mixture is formed in the enzymic hydrolysis of sucrose, which is contained in the juices collected by bees.

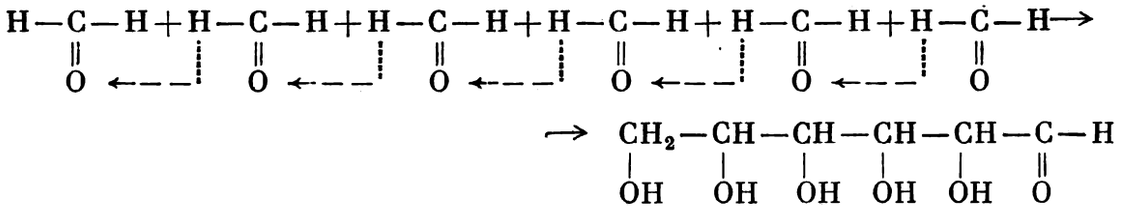
Other monosaccharides are seldom found naturally in the free state, but they are in the composition of important oligo- and polysaccharides. For example, *xylose* (*wood sugar*) is a component of the polysaccharide *xylan*, which is found together with cellulose in straw, maize stalks, and raw cotton; *arabinose* is found in plants in the form of the polysaccharide *araban*, which is in the composition of cherry gum and gum arabic (hence the name "arabinose"); *ribose* is of very great biological importance, because it is connected with nucleic acids (see Sec. 22.4); *mannose* is a component of the polysaccharides *mannans*; *galactose* is in the composition of the disaccharide *lactose*, or *milk sugar*.

The most complicated peculiarities inherent in organic compounds are found in the carbohydrate class. Monosaccharides can exist in a series of tautomeric forms. The presence of several asymmetric carbon atoms in their molecules engenders a large amount of optically active stereoisomers. For instance, a substance of the $C_6H_{12}O_6$ composition can form about a hundred structurally and spatially isomeric forms or tautomeric modifications.

Mono- and disaccharides are colourless crystalline substances which dissolve well in water. They are all optically active and have a sweet taste. Ordinary cane (or beet) sugar is a typical representative of disaccharides, and is known as *sucrose*.

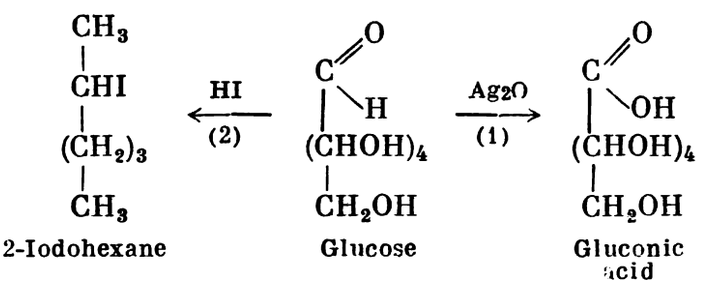
Polysaccharides are high-molecular-weight compounds. They possess properties which are characteristic of substances of such a type: they do not melt, and they form colloid solutions. A common feature of oligo- and polysaccharides is that they are capable of undergoing hydrolysis with the formation of monosaccharides.

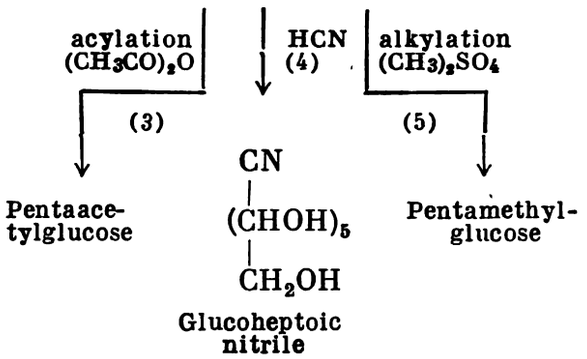
The natural source of carbohydrates is *photosynthesis* i.e., the conversion of atmospheric carbon dioxide into sugars by means of solar energy. This process occurs in green leaves in the sun. The catalyst in this case is *chlorophyll*, a green pigment of leaves. The synthetic methods of obtaining carbohydrates are of no practical importance, although they are known. A saccharide was first synthesized in 1861 by A. M. Butlerov under the action of lime water on formaldehyde. The reaction consists in the aldol condensation of several formaldehyde molecules:



MONOSACCHARIDES

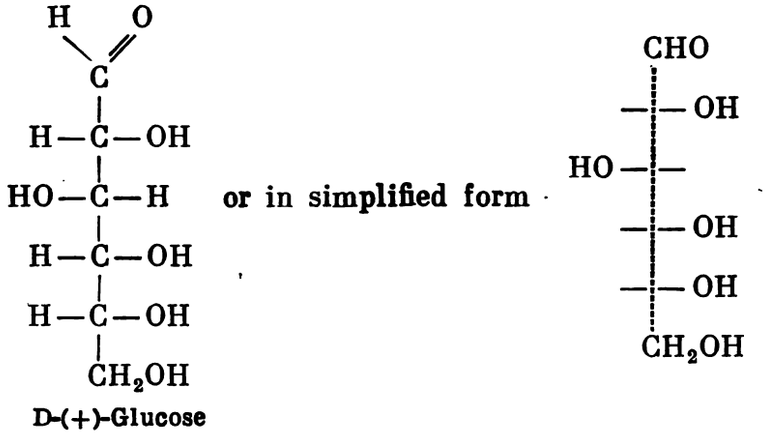
19.2. Structure. Aldehyde forms. Let us consider the structure of monosaccharides by taking the example of *glucose*. It was first obtained in 1811 by the Russian chemist G.Z. Kirchgof in starch hydrolysis. At the end of the 1860's, A.A. Kolly (Moscow University) proved that there were five hydroxyl groups in the glucose molecule. The sixth oxygen atom should apparently be in the composition of the aldehyde group, because glucose produces many qualitative reactions for the aldehyde group, i.e., it is oxidized by silver oxide (reaction 1) and adds hydrocyanic acid (reaction 4):





The presence of an unbranched chain of carbon atoms in glucose is seen from its transformation into 2-iodohexane with a normal chain of carbon atoms (reaction 2) under the action of hydrogen iodide. The fact that *pentaacetylglucose* and *pentamethylglucose* are formed as a result of acylation (reaction 3) and alkylation (reaction 5), respectively, also proves that five hydroxyl groups exist in glucose. But these derivatives are not built so simply as can be imagined from the aldehyde form of glucose. We will deal with such derivatives later.

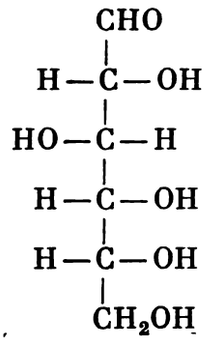
There are four asymmetric carbon atoms in the aldohexose molecule, and therefore substances of such a structure have 2^4, or 16, stereoisomers. At the end of the nineteenth century, the configuration (the arrangement of atoms in space) of natural dextrorotatory glucose was ascertained by E. Fischer in his classical works; this configuration is expressed by the following projection formula:

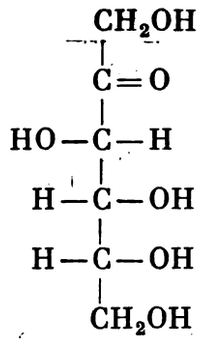


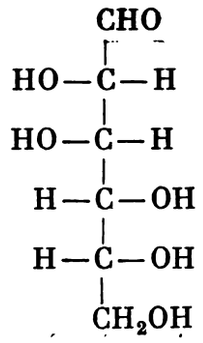
The sign (+)- indicates the direction of optical rotation, while D stands for the configuration. The notation D is given to saccharides in whose projection formula the hydroxyl of the lowest asymmetric atom is at the right.

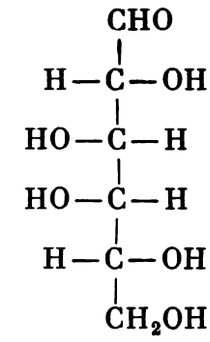
Other monosaccharides may differ from glucose by the number of carbon atoms, and may have both a keto group instead of an aldehyde one (e.g., fructose) and a different configuration of asymmetric centres. The formulas of some naturally occurring monosaccharides are given below.

Aldo- and ketohexoses:

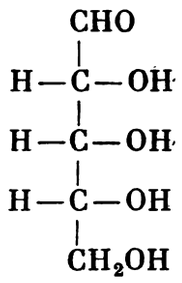

D-(+)-Glucose

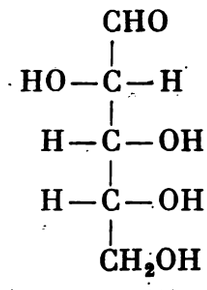

D-(−)-Fructose

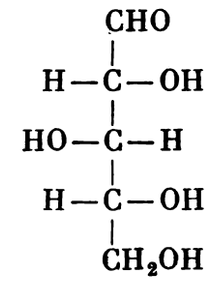

D-(+)-Mannose


D-(+)-Galactose

Aldopentoses:


D-(−)-Ribose


D-(−)-Arabinose


D-(+)-Xylose

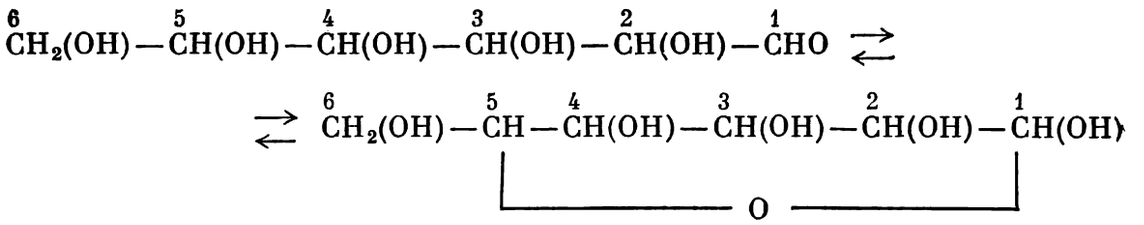
Cyclic forms. As we have already seen, some properties of monosaccharides cannot be explained by the form for aldehyde alcohol. For instance, glucose enters into not all the reactions characteristic of aldehydes, e.g., it does not form a bisulphite compound and does not produce a colouring when it reacts with fuchsin sulphurous acid. It also turned out that not all the hydroxyl groups of glucose have the same chemical properties. This is seen when methyl alcohol and hydrogen chloride act on glucose, merely *one* of its hydroxyls is methylated, while the remaining hydroxyl groups are alkylated only under more rigid conditions (methylation is effected under the action of methyl iodide and silver oxide, dimethyl sulphate and alkali). In pentamethylglucose thus obtained, one of the methyl groups is readily eliminated in hydrolysis, while the others are firmly retained.

When glucose is dissolved in water, the value of specific rotation gradually changes; this is known as *mutarotation*. The specific optical rotation of a freshly prepared aqueous solution of glucose is $[\alpha]_D$ + + 112°; when the solution is allowed to stand, rotation gradually diminishes, reaching the value of $[\alpha]_D$ + 52.5°. It was ascertained later that this final rotation is created by an equilibrium mixture of two forms: α-glucose with a rotation of $[\alpha]_D$ + 112° and β-glucose with a rotation of $[\alpha]_D$ + 18.7°. A pure α-form can be separated by crystallization from water, and a pure β-form, by crystallization

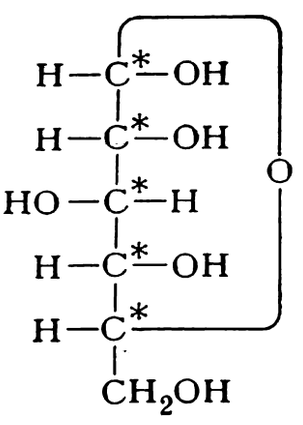
from pyridine (the essential difference between α- and β-forms is given further).

Glucose properties which cannot be explained by an aldehyde form for glucose can be explained by its *cyclic* form. This form is known also as an *oxide* or *hemiacetal* form.

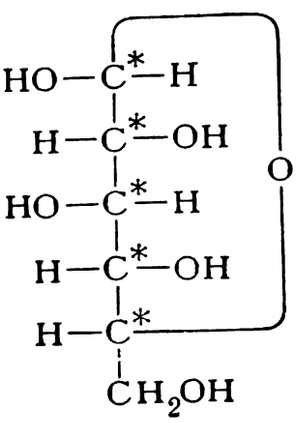
The carbon form described by the cyclic structure is a tautomeric modification which is in equilibrium with the aldehyde form:



The tautomeric interconversion of the aldehyde form to a cyclic one occurs when the hydrogen atom of the hydroxyl which is attached to the fifth carbon atom moves toward the oxygen atom of the carbonyl group. As a result, the carbon atom C-1 becomes asymmetric, while a bond is established between the atoms C-1 and C-5 through the oxygen atom (hence the term *oxide form*) with the formation of a six-membered cycle. The newly formed asymmetric carbon atom C-1 may have two antipode configurations, i.e., there may be two cyclic isomers known as α- and β-forms



α-Form of D-glucose

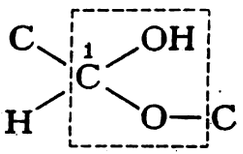


β-Form of D-glucose

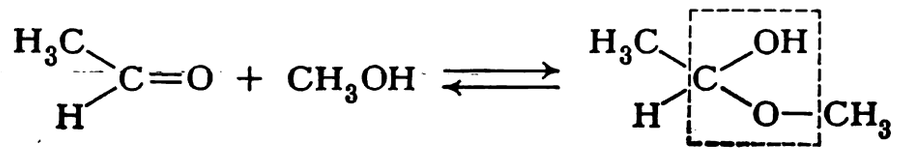
In these two *diastereomers*, the configurations of the "old" asymmetric carbon atoms are the *same*, while those of the newly formed asymmetric carbon atom are opposite. That is exactly the difference between α-glucose and β-glucose which were described above.

The hydroxyl which originated at the carbon atom C-1 during the conversion to the cyclic form considerably differs from all other hydroxyl groups. Ordinary alcoholic hydroxyls are attached to the atoms C-2-C-6, while the hydroxyl group attached to the carbon

atom C-1 belongs to the *hemiacetal* grouping (p. 220):

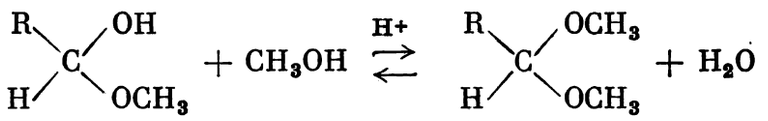


The structure of this grouping is similar to that of hemiacetals, which are engendered when a molecule of alcohol is added to aldehyde, e.g.,

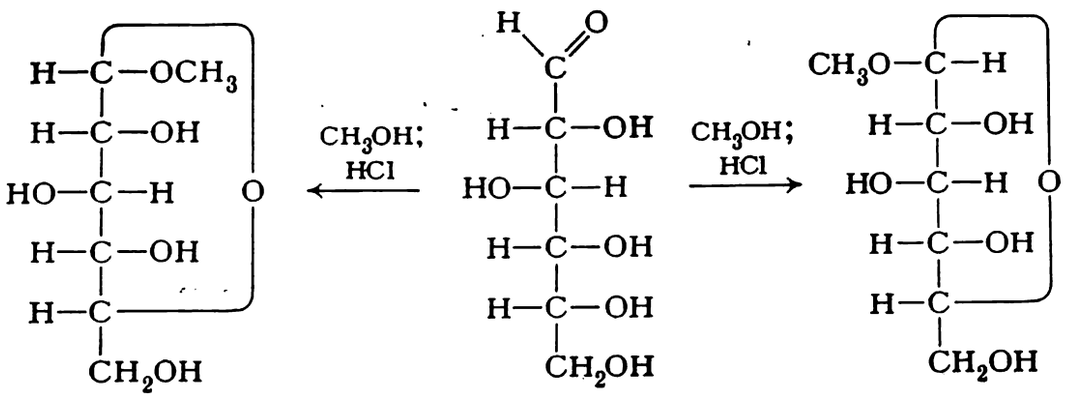


Hemiacetals are readily formed and hydrolyzed. In the case of glucose, hemiacetal formation is an *intramolecular* reaction. In glucose solutions, equilibrium is established between aldehyde and hemiacetal α- and β-forms.

Hemiacetals are transformed into *acetals* in the presence of acid catalysts:



Monosaccharides are transformed similarly. When methyl alcohol and hydrogen chloride act on them, two diastereomeric acetals, being the derivatives of the cyclic form of glucose, are formed:



α-Methyl glucoside — Glucose — β-Methyl glucoside

Such compounds are called *glycosides*, while in the case of glucose, they are called *glucosides*.

The hemiacetal hydroxyl group (at C-1 atom) is known also as a *glycoside* group. In glycosides, the hydroxyl group is replaced by the alkoxy group OR, and therefore it cannot be tautomerically

converted into an aldehyde form. Indeed, glycosides do not exhibit mutarotation.

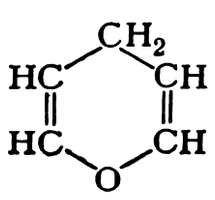
Glycosides are found naturally. Such compounds as phenols and cyanohydrins may act as an alcoholic component (the *aglycone*) in them. Glycosides include plant dyes, cardiac glycosides, which produce a strong physiological effect, and tanning agents. An example is the glycoside *amygdalin*, $C_{20}H_{27}O_{11}N$, which is contained in the grains of bitter almond and the stones of other fruits. Structurally, it is a glycoside of the disaccharide gentiobiose and the cyanohydrin benzaldehyde. In acid hydrolysis, amygdalin decomposes into carbon, benzaldehyde and hydrocyanic acid:

$$C_{20}H_{27}O_{11}N \xrightarrow{2H_2O(H^+)} 2C_6H_{12}O_6 + C_6H_5CHO + HCN$$

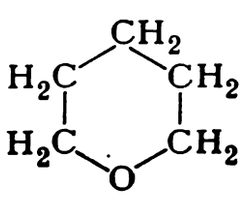
The poisonous effect which fruit stones produce when they are consumed in large amounts is due to the action of hydrocyanic acid which is separated.

Cyclic formulas written in the way which we used until now do not show the spatial structure of a molecule clearly enough. There is a much clearer way of writing them with the usual representation of a five- or six-membered ring.

Six-membered cyclic forms of monosaccharides are called *pyranose* forms, because their structure is based on the six-membered ring of pyran, a heterocyclic compound which contains the oxygen atom in the cycle:

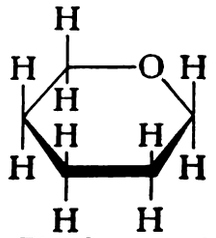


Pyran



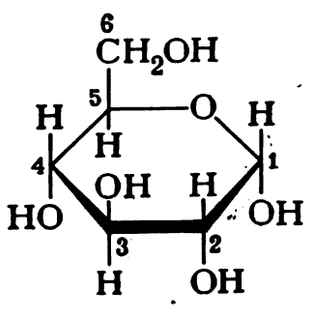
Tetrahydropyran

≡

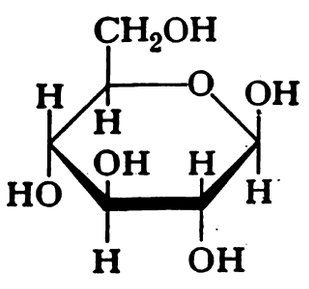


The form used for representing carbohydrates

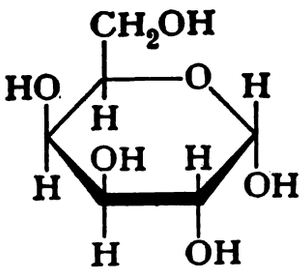
Cyclic formulas of some hexoses are given below as an example:



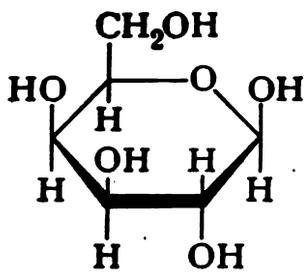
α-D-Glucose (α-D-glucopyranose)



β-D-Glucose (β-D-glucopyranose)



α-D-Galactose
(α-D-galactopyranose)



β-D-Galactose
(β-D-galactopyranose)

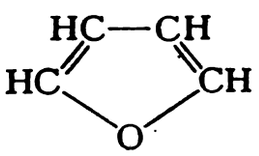
The notations α- and β- are selected in conformity with the following rules:

The sign α- is used to denote the configuration of a glycoside asymmetric centre of the saccharides of the D series, in which the glycoside hydroxyl is at the *right* in the projection formula. In the foregoing formulas with a six-membered ring, oxygen is at the remote part of the ring, while the *glycoside hydroxyl* is at the right of it. It is written *below* if it has an alpha configuration.

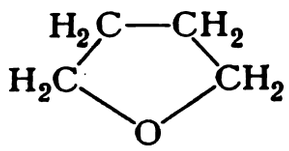
The sign β- is used to denote the configuration with the OH group of the glycoside centre at the *left*; this group will be *above* in the cyclic formula.

We represented pyranose formulas of carbohydrates as a plane six-membered ring, while actually this ring, like cyclohexane, has the chair conformation.

Five-membered cyclic forms of monosaccharides are called *furanose* forms, because they are based on a five-membered oxygen-containing ring of furan:

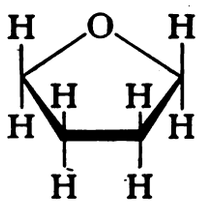


Furan



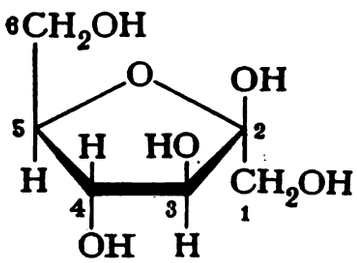
Tetrahydrofuran

≡

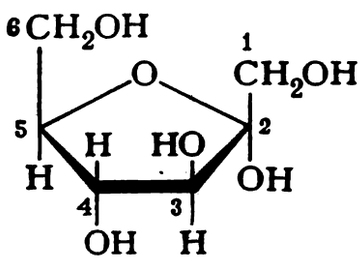


The form used for representing carbohydrates

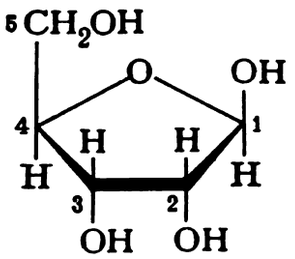
Cyclic formulas of some furanoses are given below:



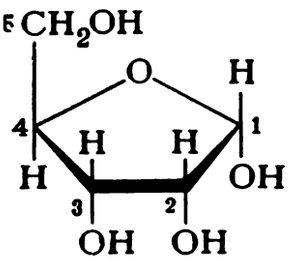
β-D-Fructose
(β-D-fructofuranose)



α-D-Fructose
(α-D-fructofuranose)



β-D-Ribose
(β-D-ribofuranose)

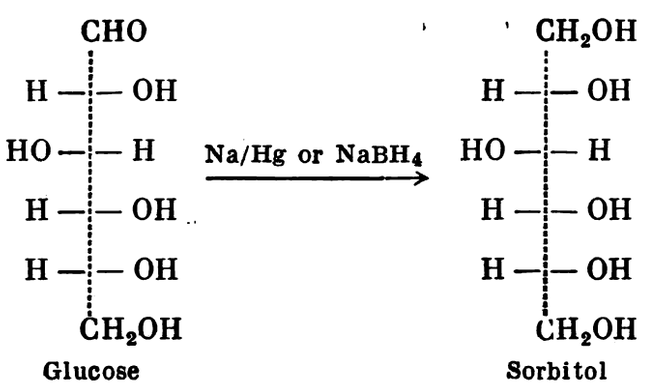


α-D-Ribose
(α-D-ribofuranose)

19.3. Chemical Properties. The chemical properties of monosaccharides can be understood more easily when their structure is known. These properties will be considered by taking mainly glucose as an example. Moreover, glucose will sometimes be represented in the aldehyde form, and sometimes in the cyclic form. Since both forms are in equilibrium with one another, tautomeric equilibrium is shifted toward the reacting form when one of the forms is spent in a reaction. Therefore, although the content of the aldehyde form is low, glucose can be completely converted into derivatives of this form. In other reactions, only the derivatives of the other tautomeric form, i.e., the cyclic form, are engendered.

Some important reactions are described below:

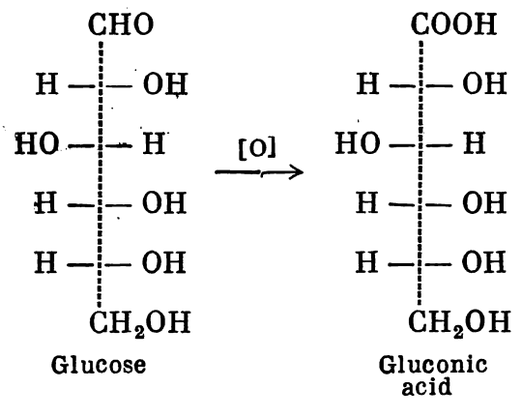
1. Reduction. Glucose is converted into the hexahydric alcohol *sorbitol* under the action of reducing agents (sodium amalgam, sodium borohydride):



Glucose Sorbitol

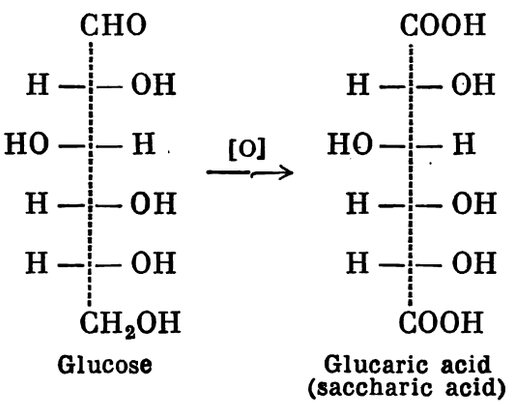
2. Oxidation. Chlorine (or bromine) water acts especially on the aldehyde group of monosaccharide, oxidizing it to the carboxyl group. The compounds thus obtained are known as *aldonic acids*,

e.g.,



Glucose — Gluconic acid

Stronger oxidizing agents (e.g., concentrated nitric acid) convert into the carboxyl not only the aldehyde group, but also the primary alcoholic group, and then dibasic acids are formed. In the IUPAC nomenclature, the name of these acids is composed on the basis of the name of the appropriate monosaccharide by replacing the suffix **-ose** with the ending **-aric acid:**



Glucose — Glucaric acid (saccharic acid)

To qualitatively detect carbohydrates, use is made of the silver mirror reaction or the action of Fehling's solution*. In this case, oxidation also occurs, but the process is a complex one and diverse products are formed. Ketoses, unlike ordinary ketones, are also oxidized by Fehling's solution.

3. Addition of hydrocyanic acid to the aldehyde group of glucose. In this case, the carbon chain is extended by one atom and a new asymmetric centre is formed. This reaction is of great importance in theoretical studies when it is necessary to pass over from lower saccharides to higher ones:

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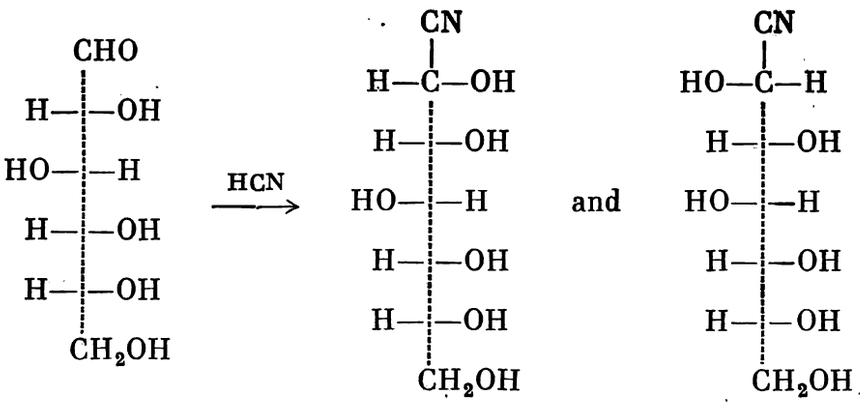
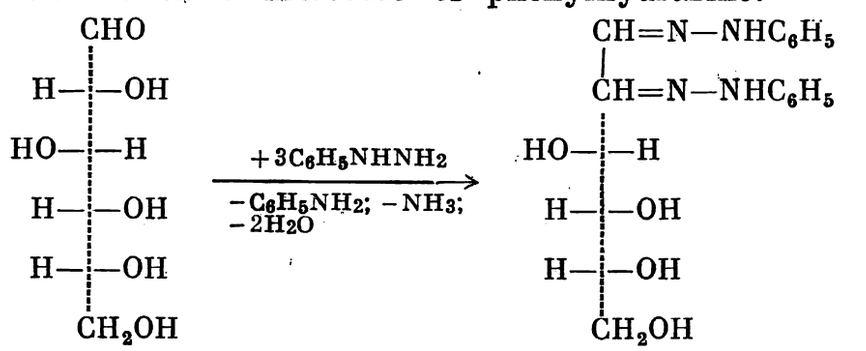
* *Fehling's solution* is prepared by mixing an aqueous solution of cupric sulphate with an alkaline solution of Seignette salt. In this case, a dark blue solution of a copper (II) tartrate complex is formed.



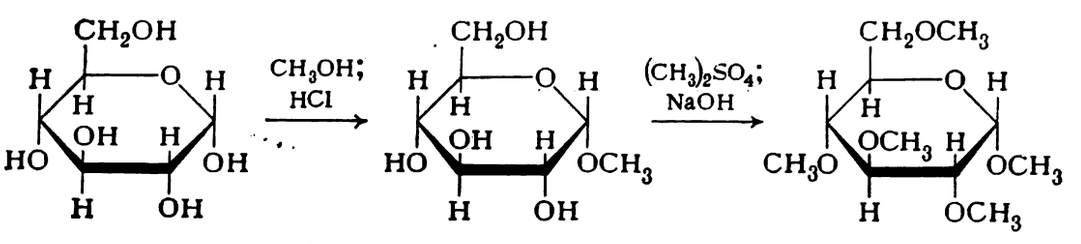
4. Reaction with phenylhydrazine. When glucose is heated with excess phenylhydrazine, its aldehyde group reacts at first and the product of the replacement of carbonyl oxygen by the phenylhydrazine residue is formed (see Sec. 11.4). The second molecule of phenylhydrazine acts as an oxidizing agent, converting the adjacent to the aldehyde group hydroxyl into a carbonyl group, which reacts ordinarily with the third molecule of phenylhydrazine:



Glucose — Glucosazone

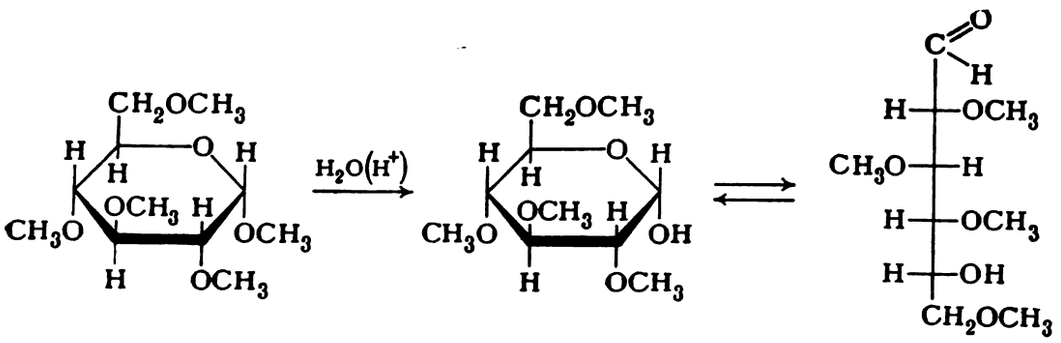
Osazones are yellow crystals whose shape and melting point make it possible to ascertain the carbon from which osazone is obtained. Therefore, osazones are of great importance in saccharide identification. When osazone is formed, the asymmetric centre nearest to the carbonyl group disappears, and therefore glucose and mannose, for example, form the same osazone.

5. Alkylation. When alkylating agents act on glucose, its ethers which are derivatives of the cyclic form can be obtained. As we have already seen (p. 388), the glycoside hydroxyl reacts most readily:



α-D-Glucose — α-O-Methyl-D-glucoside — Penta-O-methyl-α-D-Glucose

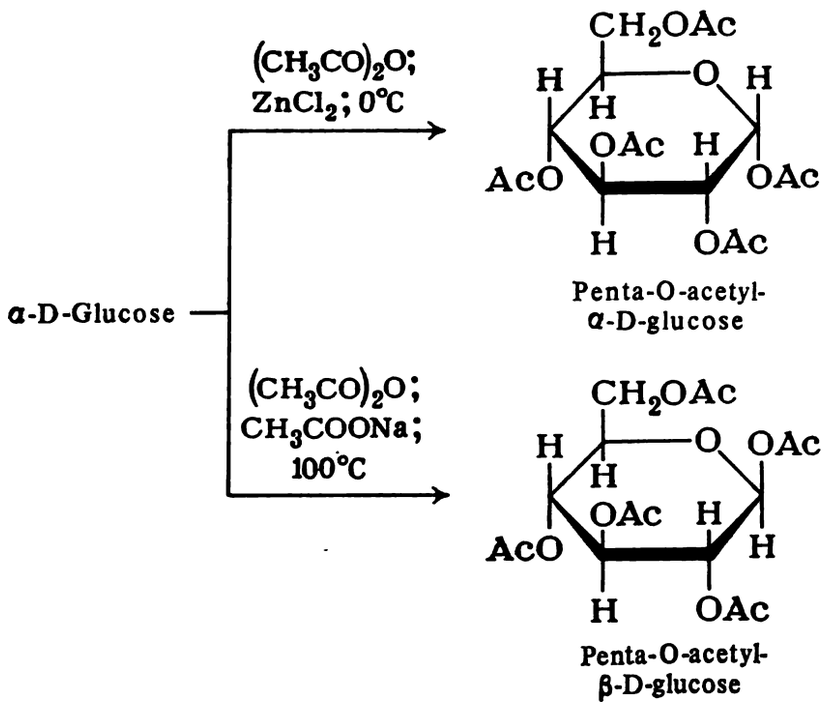
One of the methyl groups of pentamethylglucose, i.e., the one which is *bonded with the glycoside hydroxyl*, is capable of being readily eliminated in hydrolysis with dilute acids. Tetramethylglucose is then formed:



Since the glycoside hydroxyl of tetramethylglucose is free, it can assume a noncyclic form and, consequently, enter into reactions which are characteristic of the aldehyde group (reduction, oxidation, HCN addition) and exhibit mutarotation.

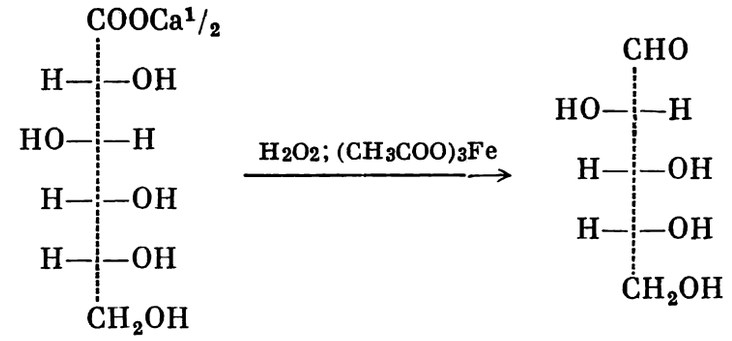
Pentamethylglucose is incapable of being converted into a noncyclic form and does not produce the above-mentioned reactions.

6. Acylation. Hydroxyl groups of glucose are readily converted into ester ones under the action of acylating agents. This occurs, for example, under the action of acetic anhydride. The derivatives of the α- or β-forms of glucose can be obtained, depending on the conditions under which a reaction occurs:



7. The shortening of the carbon chain of a carbohydrate by eliminating a carbon atom from the "aldehyde end" of the molecule. In these reactions, hexoses are converted into pentoses, e.g., glucose into arabinose.

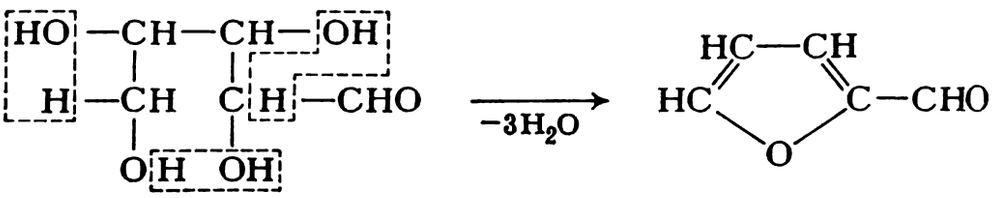
There are several ways of carrying out this reaction. One of them is the Ruff degradation, which consists in the oxidation of the calcium salt of aldonic acid by hydrogen peroxide in the presence of ferric acetate:



Calcium gluconate D-Arabinose

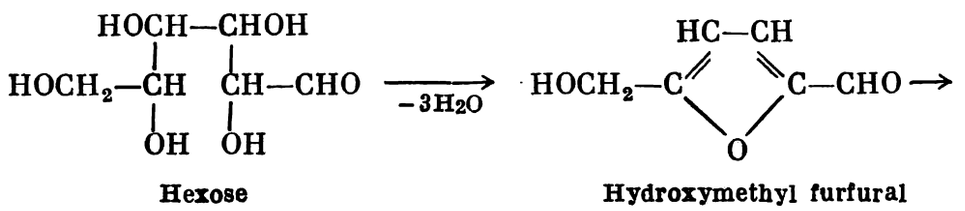
8. Action of bases. Monosaccharides are *epimerized* under the action of weak bases. Epimerization is inversion of the configuration at the asymmetric carbon atom (carbon-2) adjacent to the aldehyde group. At the same time, aldoses and ketoses are interconverted. For instance, if lime water is added to glucose, it will be converted in five days into an equilibrium mixture containing 63.5 per cent of glucose, 31 per cent of fructose and 2.5 per cent of mannose. Strong bases decompose monosaccharides.

9. Action of acids. Pentoses and hexoses act differently toward acids. When pentoses are heated with mineral acids, water is eliminated from them and furfural is formed:



Pentose Furfural

In a similar reaction, hexoses yield at first unstable hydroxymethyl furfural, which then decomposes with the formation of levulinic and formic acids:



Hexose Hydroxymethyl furfural

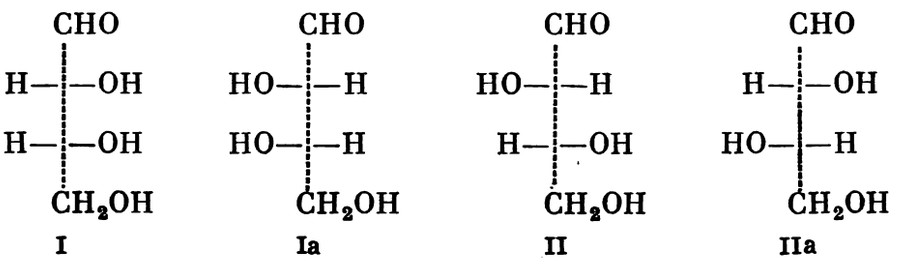
$$\longrightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}COOH + HCOOH$$

Levulinic acid — Formic acid

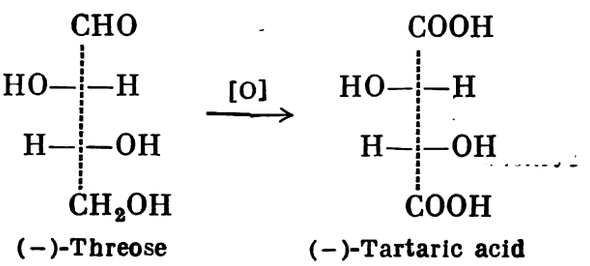
Furfural can be detected by means of a colour reaction with phloroglucinol (1,3,5-trihydroxybenzene), and thus pentoses can be distinguished from hexoses.

10. Alcoholic fermentation. This reaction is characteristic of hexoses. It is effected under the action of biological catalysts called *enzymes*. In fermentation, hexoses are converted into ethyl alcohol (see Sec. 10.5). Fermentation is not characteristic of pentoses.

19.4. Stereochemistry of Monosaccharides. The presence of several asymmetric carbon atoms creates conditions for the existence of a large number of stereoisomeric monosaccharides. For instance, glucose is a member of a large family of 16 aldohexoses $C_6H_{12}O_6$. Arabinose is one of the eight stereoisomeric aldopentoses. Aldotetroses form two diastereomeric pairs, i.e., (—)- and (+)-erythrose (formulas I and Ia) and (—)- and (+)-threose (formulas II and IIa):



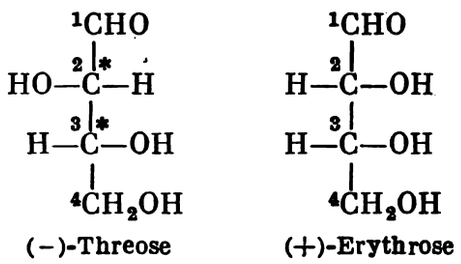
To determine the configuration of tetroses, it is necessary to know the projection formulas for (+)- and (—)-erythrose and (+)- and (—)-threose. The configuration of (—)-threose follows from its conversion into (—)-tartaric acid on oxidation. In this reaction, the terminal groups CHO and CH_2OH are converted into carboxyl COOH groups, while the central part of the molecule (asymmetric atoms with their bonds) is unaffected:



Therefore, it may be asserted that the three-dimensional arrangement of substituents around asymmetric atoms of (—)-threose is the same as that of (—)-tartaric acid, whose configuration has been reliably ascertained by the X-ray method.

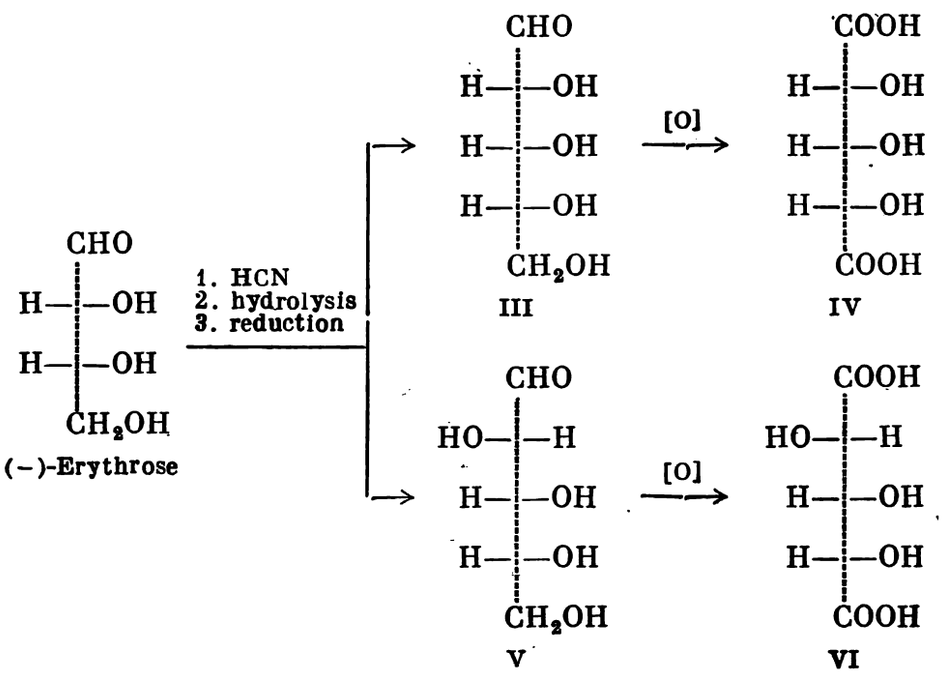
The configuration of (—)-erythrose can be substantiated by the fact that the same (+)-glyceraldehyde is obtained from (—)-threose

and (—)-erythrose when the chain is shortened (p. 395). This means that the configurations of the "lower" asymmetric atom of (—)-threose and (—)-erythrose are the same, and that they differ only by the configuration of the "upper" asymmetric atom, which disappears in degradation to glyceraldehyde. Proceeding from this, the projection formula of (—)-erythrose can be written as:



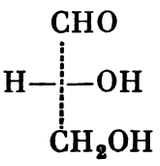
(—)-Threose and (—)-erythrose form a pair of diastereomers whose configuration of the asymmetric centres of C-3 is the same, while the configuration of the asymmetric centres of C-2 is the opposite.

Cyanohydrin synthesis (p. 393) can be used to obtain two pentoses (III and V) from (—)-erythrose; these pentoses differ from one another by the configuration of the newly formed "upper" asymmetric atom. Pentose III is known as (—)-ribose, while pentose V, as (—)-arabinose. They differ from one another (this difference is important for ascertaining the configuration) by the fact that (—)-ribose produces a *meso-form* of trihydroxyglutaric acid IV, while (—)-arabinose, *optically active* trihydroxyglutaric acid VI:



(—)-Arabinose V can be converted into a mixture of two hexoses by a further building by means of cyanohydrin synthesis; these hexoses will also differ from one another by the configuration of the newly formed asymmetric centre. Similar considerations can be used to prove that these hexoses [(+)-glucose and (+)-mannose] correspond to the projection formulas given earlier (p. 386).

In accordance with M. A. Rozanov's proposal (1905), all the saccharides whose configuration of the "lower" asymmetric carbon atom (which is the most remote from the aldehyde group) coincides with that of dextrorotatory glyceraldehyde



D-(+)-Glyceraldehyde

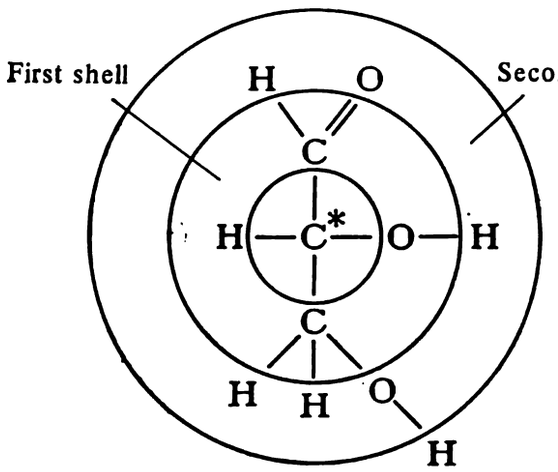
are related to the D-saccharide series. We have often used this notation.

D-glyceraldehyde is the key substance for denoting the saccharide configuration. In practice, the "key" system is convenient for denoting configurations within the limits of a group of chemically related compounds (or, in other words, within the limits of a *steric series*). But, in general, this system has many disadvantages. One of them is that the notation L- or D- applies only to one "key" asymmetric atom in complex substances having several asymmetric atoms. For example, the name "D-glucose" shows only that the hydroxyl of the lower asymmetric carbon atom is on the right of the projection formula, but it does not indicate the configuration of the remaining three asymmetric atoms.

A system for denoting the configuration of the asymmetric atom that is independent of the "key" had been proposed by A. P. Terentyev and his coworkers in the Soviet Union in the early 1950's; similar proposals had been made outside the Soviet Union by Cahn, Ingold and Prelog. Both systems describe the three-dimensional structure proper, i.e., the volumetric model of a molecule, and not the projection formulas.

According to the *Cahn-Ingold-Prelog* (*CIP*) *sequence rule*, the atomic numbers of the atoms constituting the substituents are counted in order to determine substituent priority. Let us consider the rules of counting them by taking the example of glyceraldehyde

and writing its formula in the following way:



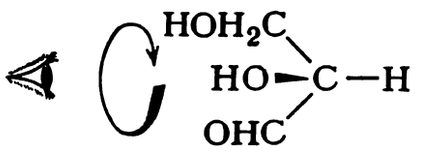
Substituent	CHO	OH	CH_2OH	H
Sum of atomic numbers				
first shell	6	8	6	1
second shell	$1+2\times8$	—	$2\times1+1\times8$	—

The atomic numbers of atoms which are directly linked with the asymmetric centre (atoms of the first shell) indicate that the OH group whose atomic number of oxygen is 8 is the highest, and the hydrogen atom, the lowest, in priority in this group. The groups CHO and CH_2OH have the same atom (carbon) with the atomic number 6 in the first shell, and therefore the atomic numbers in the second shell are summed up in order to determine the priority of the groups. This summation gives the number 17 for the CHO group (the atom linked by a double bond is counted twice) and the number 10 for the CH_2OH group. Thus, the substituents at the asymmetric atom of glyceraldehyde are arranged in the following series according to the priority of atomic numbers:

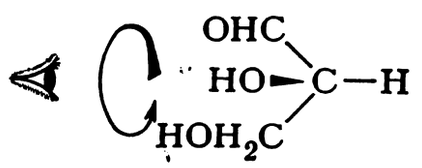
$$OH > CHO > CH_2OH > H$$

To determine the stereochemical notation according to the Cahn-Ingold-Prelog rule, the model is so arranged that the substituent which is attached to the asymmetric atom and is the lowest in priority would be the most remote from the observer, while the remaining three substituents would be in the tetrahedron base, which is turned toward the observer: the configuration is denoted by the letter S when the priority of the groups diminishes counterclockwise, and

by the letter R when it diminishes clockwise, e.g.,



R-Configuration;
(+)-Glyceraldehyde



S-Configuration;
(−)-Glyceraldehyde

The R,S system is the basis of the stereochemical nomenclature adopted by the IUPAC Commission in 1969.

OLIGOSACCHARIDES

19.5. Structure and Properties. As we have already seen, glycosides are formed when monosaccharides with alcohols are heated in the presence of acid catalysts. The second monosaccharide molecule can act as an alcoholic component in this reaction. As a result of this reaction, water is eliminated from two monosaccharide molecules and *disaccharide* is formed:

$$2C_6H_{12}O_6 \xrightarrow[-H_2O]{} C_{12}H_{22}O_{11}$$

Trisaccharide is obtained similarly from three monosaccharide molecules:

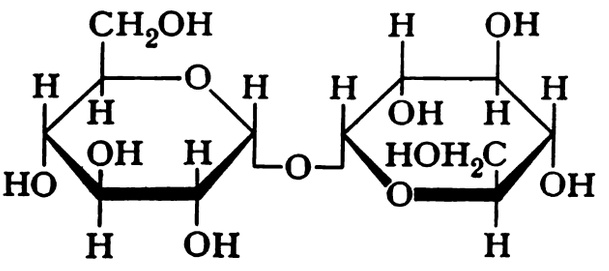
$$3C_6H_{12}O_6 \xrightarrow[-2H_2O]{} C_{18}H_{32}O_{16}$$

Similar compounds composed of a small number of monosaccharide residues (2-6) are called *oligosaccharides.*

The most important oligosaccharides are *disaccharides.* They can be very different structurally: they can include residues of different monosaccharides, and different hydroxyl groups can participate in the formation of a bond between these residues. Disaccharide molecules include cyclic forms of monosaccharides: they can be pyranose or furanose with an alpha or beta configuration of the glycoside hydroxyl.

There are two types of disaccharides, and the difference between them depends on whether *both glycoside hydroxyls* or *one glycoside hydroxyl* and *one alcoholic* hydroxyl participate in the formation of a bond. An example of disaccharides of the first type is *trehalose*

(the bond is of a glycosido-glycoside type):



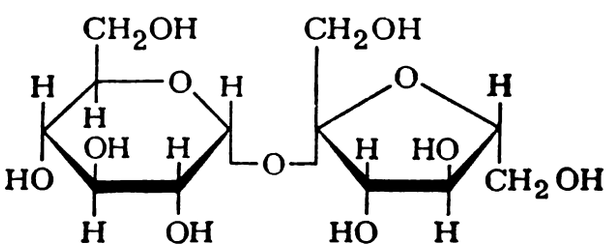
α-D-Glucose residue α-D-Glucose residue

Trehalose

(α,α-glucosidoglucose)

There are no free glycoside hydroxyls in disaccharides of such a type. They are incapable of passing over into a tautomeric aldehyde form, and therefore they cannot enter into reactions which are characteristic of this form. For instance, disaccharides of the *glycosido-glycoside type* do not produce the silver mirror reaction, which is characteristic of monosaccharides, and do not reduce Fehling's solution. Therefore, they are known as *non-reducing disaccharides*. Such disaccharides are capable of entering only into reactions which are engendered by the presence of hydroxyl groups (alkylation and acylation).

Trehalose, being given above as an example, is structurally the simplest nonreducing disaccharide, because it consists of two same units of *α-D-glucose*. But trehalose is not very important naturally, as it is found only in mushrooms, yeasts, and some plants. Another nonreducing disaccharide, *sucrose* (ordinary sugar), being structurally more complex and consisting of the units of glucose and fructose, is of far greater importance:



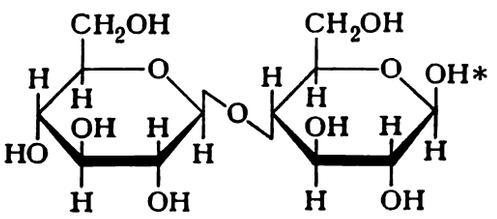
α-Glucose residue β-Fructose residue

Sucrose

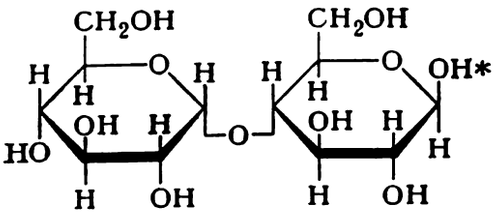
(α-glucosido-β-fructoside)

There is another type of disaccharides: disaccharides of the *glycosidoglycose type*, or *reducing disaccharides*. The most important natural products, i.e., cellobiose, maltose and lactose, belong to this type. *Cellobiose* and *maltose* consist of glucose units and differ from one another by the fact that the bond between monosaccharide units is of the β-glycoside type in the cellobiose molecule, and of the α-glycoside type in the maltose molecule. Units of glucose and

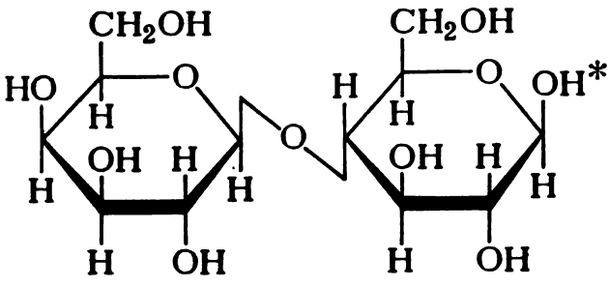
galactose are in the composition of the disaccharide called *lactose* (milk sugar).



Cellobiose
[4-(β-glucosido)-glucose]



Maltose
[4-(α-glucosido)-glucose]



Lactose
[4-(β-galactosido)-glucose]

All the disaccharides of this type have a free glycoside hydroxyl (it is marked with an asterisk in the formulas); consequently, they can pass over into the aldehyde form, and hence their reducing properties. Reducing disaccharides enter into the same chemical reactions as monosaccharides; they are capable of both forming alkyl and acyl derivatives at the expense of their hydroxyl groups and being oxidized to monocarboxylic acids (of the gluconic type); they can yield osazones, produce the silver mirror reaction, and separate cuprous oxide from Fehling's solution.

A characteristic feature of disaccharides (like oligosaccharides and polysaccharides in general) is the ability of being converted into monosaccharides in acid or enzymatic hydrolysis. Sucrose hydrolysis is accompanied by a change in the sign of optical rotation: dextrorotatory saccharose becomes a levorotatory mixture of glucose and fructose. This process is often called *inversion*.

The most important disaccharide, *sucrose*, is very widely distributed naturally. "Sucrose" is the chemical name of ordinary sugar, which is also known as *cane* or *beet* sugar. It is obtained from sugarcane, which grows in the tropics (in Cuba and other countries of Central America), or from sugar beet (which contains 12-15 per cent of sucrose).

Sugar beet is sliced into cossettes, and then sucrose is extracted from them by hot water in special devices called diffusers. The solution obtained is treated with lime in order to precipitate impurities (defecation), while excess calcium hydroxide which has partially

passed into solution is precipitated by passing through carbon dioxide (saturation). When the precipitate is separated, the solution is evaporated in vacuum devices. This is how fine-crystalline raw sugar is obtained. After it is additionally purified, refined sugar is obtained. Depending on crystallization conditions, it is separated as either fine crystals or compact "sugar loafs", which are broken or sawn into pieces. Rapidly dissolving block sugar is made by pressing finely ground sugar into blocks.

POLYSACCHARIDES

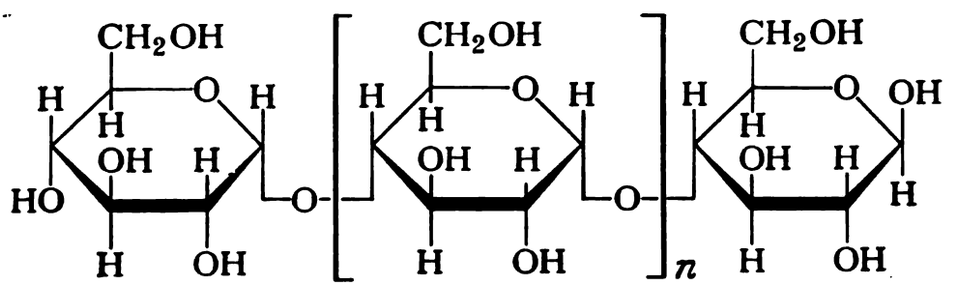
Polysaccharide molecules can be regarded as the condensation products of a large number of monosaccharide molecules together. Their composition is expressed by the formula $(C_6H_{10}O_5)_n$, where n reaches the values of hundreds or thousands. The most important polysaccharides are starch and cellulose.

19.6. Starch. Starch is formed in plants by photosynthesis and is deposited in roots, tubers and seeds. The grains of rice, wheat, rye and other cereals contain 60-80 per cent of starch, while potato tubers contain 15-20 per cent of it. In the animal kingdom, the polysaccharide called *glycogen*, which is related to starch and is deposited mainly in the liver, acts as "reserve carbohydrate".

Starch is a white substance which consists of fine granules. It is insoluble in cold water, and swells and gradually dissolves in hot water. The viscous solutions formed become a gelatinous mass when temperature drops.

Starch is a mixture of the polysaccharides called *amylopectin* and *amylose*. Pure, crystalline amylose can be separated from starch by special treatment with solvents. Pure amylose does not form paste on swelling, and it gives a dark blue colour with iodine. Amylopectin is responsible for paste formation, and it gives only a slight violet colour with iodine.

Both amylose and amylopectin consist of glucose residues which are linked by α-glycoside bonds, but they differ from one another by *molecular shape*. Amylose is a *linear* polysaccharide which is composed of several thousand glucose residues linked by the α-glycoside bond. The amylose structure is schematically illustrated by the following formula:



X-ray diffraction analysis shows that the amylose molecule is coiled into a spiral. A channel with a diameter of about 0.5 nm remains inside the spiral-like molecule, and molecules of a suitable size can be arranged in this channel; in this case, special complexes, known as *inclusion compounds* (see p. 294), are formed. One of them is the above-mentioned dark-blue compound of amylose and iodine.

The amylopectin molecule, unlike amylose, has a *branched* structure whose shape is close to a spherical one. The molecular mass of amylopectin, being determined by physical methods, has a value of the order of 10^6, i.e., the degree of polymerization is equal to about 6000.

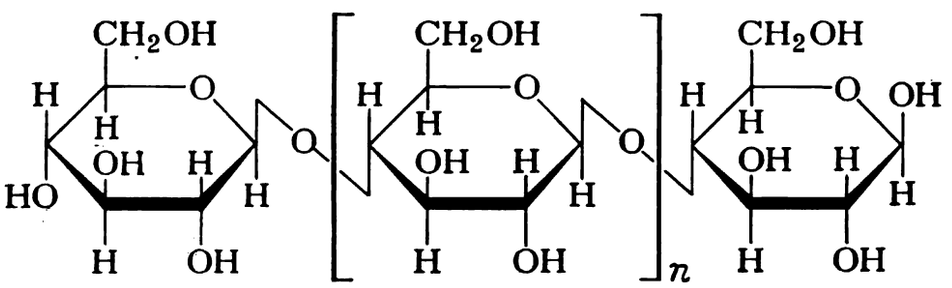
Starch utilization. The enzymatic hydrolysis of starch is important in the industrial production of ethyl alcohol from grain or potato (see Sec. 10.5). The process begins with the conversion of starch into glucose, which is then fermented.

Fermentation can yield butyl alcohol, acetone, lactic, citric and gluconic acids, and so forth, when special types of yeasts are used and conditions are changed. Glucose can be obtained as either a pure crystalline preparation or a coloured noncrystallizing *syrup* by subjecting starch to acid hydrolysis.

Starch is of the greatest importance as a food product, i.e., bread, potatoes and groats, and it is the main source of carbohydrates in our nourishment. In addition, pure starch is used in the food industry to produce confectionary, delicatessen and sausages. Much starch is used for *sizing* textiles, pasting paper and cardboard, and producing starch gum.

In analytical chemistry, starch is used as an indicator in the iodometric method of titration. To this end, it is better to employ purified amylose, because its solutions do not thicken, while the colour formed with iodine is more intense.

19.7. Cellulose. Cellulose is a polysaccharide composed of glucose units. Its structure is similar to that of amylose, i.e., it also consists of glucose residues, but they are linked with one another by β-glycoside bonds, and not, like in amylose, by α-glycoside bonds



The molecular mass of cellulose is very great, being of the order of 500,000, but it can reach even several millions; in the given formula, n is equal to tens of thousands.

Cellulose is the main "construction material" of plants, the plant cell walls being made out of it. For example, 98 per cent of the fibre of the cotton plant, or simply cotton, is cellulose. Cellulose does not melt or pass over to a vapour state, and it decomposes and becomes charred when heated to ca. 350°C. It is insoluble in water and most of the other inorganic and organic solvents.

The inability of cellulose to dissolve in water is an unexpected property of a substance which has three hydroxyl groups for every six carbon atoms. Polyhydroxyl compounds usually readily dissolve in water.

Cellulose is insoluble, because its fibers are "bundles" of parallel thread-like molecules linked by multiple hydrogen bonds, which are formed as a result of interaction between hydroxyl groups. A solvent cannot penetrate into such a "bundle", and therefore molecules are not torn away from one another.

Cellulose dissolves in an ammoniacal solution of cupric hydroxide (Schweitzer's reagent). A concentrated solution of zinc chloride and concentrated acids (sulphuric and phosphoric acids) also dissolve cellulose, but then it partially decomposes (it is hydrolyzed) with a diminution of molecular mass.

The chemical properties of cellulose are determined above all by the presence of hydroxyl groups. Cellulose trisodium alkoxide $[C_6H_7O_2(ONa)_3]_n$ can be obtained under the action of metallic sodium. *Mercerization*, or the partial formation of cellulose alcoholates, occurs under the action of concentrated aqueous solutions of alkalies, and is widely employed in the textile industry for imparting a silky lustre and better dye affinity to fabrics. A certain amount of carbonyl and carboxyl groups appears in the cellulose macromolecule as a result of oxidation. The macromolecule decomposes under the action of strong oxidizing agents. The hydroxyl groups of cellulose are capable of being alkylated and acylated with the formation of ethers and esters.

Cellulose utilization. Man has used cellulose from time immemorial. At first, wood was used as fuel and construction material, and later, cotton, flax and other fibres began to be employed as raw material for textiles. The first industrial methods of chemically treating cellulose originated as the paper industry developed.

Paper is a thin layer of cellular tissues which have been pressed and pasted together in order to lend it mechanical strength and a smooth surface so as to prevent ink from spreading.

At first, paper was made out of raw plant material from which the necessary fibres could be obtained purely mechanically: rice stems (rice paper) and cotton. Rags collected from people were also used. But these sources of raw material could not meet the growing demand for paper as book publishing developed. Especially much paper is used for printing newspapers, whose quality (whiteness,

strength and durability) is unimportant. Since about 50 per cent of wood is cellular tissue, pulverized wood began to be added to the paper mass. Such paper is not strong, and it rapidly turns yellow (especially in the light).

Different methods of chemically treating wood were proposed so as to improve the quality of wood additives to the paper mass; cellulose which is more or less free of impurities, i.e., lignin, resins, and so forth, can be obtained from wood by these methods. Several methods of separating cellulose were also proposed; let us consider the *sulphite method*, according to which pulverized wood is "boiled" with calcium bisulphite under pressure. In this case, impurities dissolve, and cellulose is filtered off. The *sulphite liquors* formed are waste products of the paper industry. But since, besides other substances, they contain monosaccharides, which are capable of fermenting, they are used as raw material for obtaining ethyl alcohol (*hydrolysis alcohol*, p. 185).

Cellulose is not only raw material in paper production. It is chemically treated further. Cellulose ethers and esters are of the greatest importance. *Cellulose nitrates* are obtained when a mixture of nitric and sulphuric acids acts on cellulose. They are all flammable and explosive. The maximum number of nitric-acid residues which can be introduced into cellulose is 3 per glucose unit:

$$[C_6H_7O_2(OH)_3]_n \xrightarrow{HNO_3} [C_6H_7O_2(ONO_2)_3]_n$$

According to the formula, the total esterification product, i.e., *cellulose trinitrate*, should contain 14.1 per cent of nitrogen. But in fact a product with a lower nitrogen content (12.5-13.5 per cent) is obtained, being known commercially as *pyroxylin*. Pyroxylin becomes gelated when it is treated with ether, and a compact mass remains when the solvent is evaporated. This mass is cut into small pieces, which are called *smokeless powder*.

The nitration product, which contains about 10 per cent of nitrogen, corresponds to *cellulose dinitrate* by its composition; commercially, this product is known as *colloxylin*. A viscous solution called *collodion*, used in medicine, is formed when a mixture of alcohol and ether acts on colloxylin. If camphor (0.4 part of camphor per part of colloxylin) is added to such a solution and the solvent is evaporated, a transparent flexible film known as *celluloid* remains. Historically, this is the first known type of plastics. Celluloid had been widely used even in the nineteenth century as a convenient thermoplastic material for producing many articles (toys, haberdashery, etc.). Celluloid is especially important in the production of motion-picture film and nitrocellulose varnish. A great disadvantage of this material is its high flammability, and therefore it is now being replaced more and more by other materials, such as *cellulose acetates*.

Cellulose triacetate is formed when a mixture of acetic anhydride and acetic acid, using sulphuric acid or zinc chloride as catalysts, acts on cellulose:

$$[C_6H_7O_2(OH)_3]_n \xrightarrow{(CH_3CO)_2O} [C_6H_7O_2(OCOCH_3)_3]_n$$

The partial acetylation of cellulose or the partial hydrolysis of triacetate engenders *secondary acetate* (2.4-2.7 residues of acetic acid per elementary unit). Cellulose acetates are used for making laquers, nonflammable motion-picture film, and acetate fibre.

When the fibres of the chief natural textile materials, i.e., cotton, wool and natural silk, are examined under the microscope, it will be seen that the first two materials differ from the third one. The fibres of cotton and wool have a "hairy" surface; on them, short hairs stick out in all directions. Silk fibres are smoother, and hence the lustre and close weave of silk textiles. Therefore, efforts to create artificial silk have long been made by changing the nature of the surface of cellulose fibres.

To obtain fibre from cellulose acetate, the latter is dissolved in a mixture of acetone and ethyl alcohol (or in a mixture of alcohol and benzene), and then the solution is pressed through (*fibre moulding*) a *spinnerette*, which is a vessel with small holes. Very thin streams which flow out of the vessel become very thin threads when the solvent evaporates (*dry spinning*), and then the threads are twisted into a thicker rayon thread, which can be woven. This type of man-made fibre has several advantages over other artificial silks, such as *viscose rayon* (see further). Therefore, its production is growing now.

The general principle of obtaining rayon (dissolution, and then thread moulding) can obviously be realized in a different way, i.e., cellulose solutions can be obtained in another way. The *viscose process* is of great technological importance. It consists in the formation of a water-soluble compound of cellulose as carbon disulphide and alkali act on it:

$$[C_6H_7O_2(OH)_3]_n \xrightarrow{CS_2;\ NaOH} \left[C_6H_7O_2\left(O{-}C\begin{matrix} \overset{S}{\parallel} \\ \diagdown SNa \end{matrix} \right)_3 \right]_n$$

The compound formed is *cellulose xanthate*. The aqueous (alkaline, to be more exact) solution of cellulose xanthate (*viscose*) is pressed through spinnerettes into a spinning bath containing sulphuric acid (*wet spinning*). Xanthate groups are eliminated under the action of the acid, and cellulose is regenerated in the form of very fine filaments of viscose rayon.

Staple fibre is also such a thread, but it is only thicker and is cut into small pieces; textiles which are substitutes for cotton fibres are obtained from it.

If viscose is pressed through narrow slits instead of spinnerettes, a transparent film known as *cellophane* is obtained.

A proposal had been made to obtain man-made fibre also from solutions of cellulose in Schweitzer's reagent. Cuprammonium rayon thus obtained is of good quality, but it costs much.

Cellulose ethers are also used in technological processes now. For instance, *methyl cellulose* is obtained by treating cellulose at first with alkali, and then with methyl chloride (under pressure):

$$[C_6H_7O_2(OH)_3]_n \xrightarrow{NaOH;\ CH_3Cl} [C_6H_7O_2(OH)(OCH_3)_2]_n$$

In methylation, cellulose becomes somewhat soluble in water; it is used mainly as a thickening agent instead of starch in the textile, cosmetic and food industries.

Ethyl cellulose is obtained similarly, and is used for producing strong frostproof films.

Artificial, cellulose-based fibres account for a large part of textile raw material.

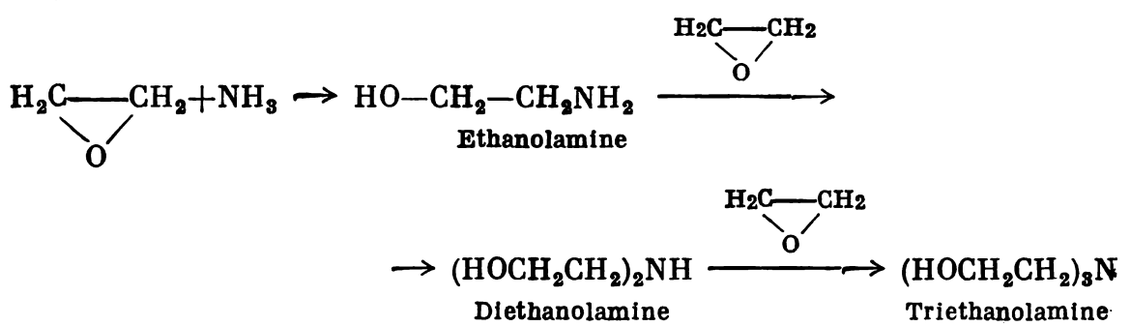
Chapter 20

AMINOALCOHOLS AND AMINO ACIDS

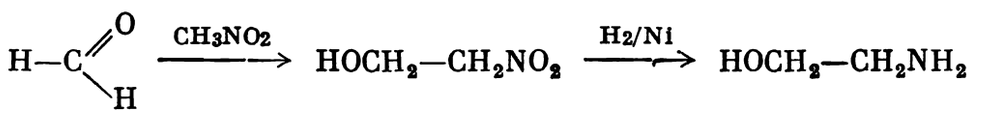
Aminoalcohols are compounds whose molecule simultaneously contains amino and hydroxyl groups, while *amino acids* are compounds with amine and carboxyl functions.

AMINOALCOHOLS AND AMINOPHENOLS

20.1. Aminoalcohols. The most important representatives of this class, *ethanolamines*, are obtained industrially from ammonia and ethylene oxide:



Nitro alcohols, which are obtained by condensing nitro compounds with aldehydes and ketones (see Sec. 14.3), form aminoalcohols in reduction:



Ethanolamines are high-boiling liquids which mix with water in all proportions. They are used as solvents. All these compounds acquire basic properties. Triethanolamine with acids forms salts, e.g.,

$$(HOCH_2CH_2)_3N + H_2S \longrightarrow (HOCH_2CH_2)_3N \cdot H_2S$$

On heating, the salt of hydrogen sulphide decomposes. This property is used for removing hydrogen sulphide from various industrial gases. Hydrogen sulphide formed can be employed, for instance, as raw material for producing sulphuric acid, while regenerated triethanolamine can be used again for gas stripping. Similarly,

triethanolamine binds carbon dioxide and hydrogen cyanide, and this is used in gas stripping as well.

Ethanolamines are used also for producing synthetic detergents. Ethanolamines are found in natural substances, too.

A nitrous analogue of yperite, $(ClCH_2CH_2)_2NH$, is formed when a halogen is substituted for hydroxyl groups in diethanolamine. It is a very poisonous liquid. Researchers once considered using compounds of such a type as preparations for treating malignant tumours.

The aminoalcohol called *choline* is an important physiologically active substance. It is structurally a quaternary ammonium base:

$$[HOCH_2CH_2—N(CH_3)_3]^+ [OH]^-$$

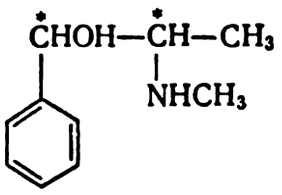
Choline is in the composition of phosphatides, which relate to fatty substances (see Sec. 12.22). Since it is capable of participating in metabolic control, synthetic choline began to be used as an additive to fodder in livestock-breeding and poultry farming.

When choline is dehydrated, a very poisonous unsaturated amine called *neurine* is formed:

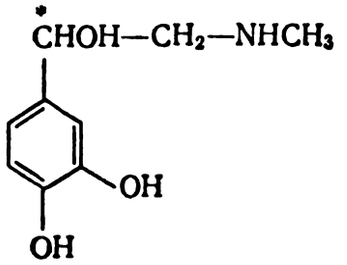
$$[CH_2=CH—N(CH_3)_3]^+ [OH]^-$$

The process occurs particularly when proteins decay.

Some aminoalcohols, i.e., benzene derivatives in which the amino group and hydroxyl are in the side chain, are also important physiologically active substances. For example, *ephedrine*, being found in some types of plants, is used as a medicinal which stimulates the central nervous system and narrows the vessels. Its molecule has two different asymmetric carbon atoms, and therefore it exists as four (2^2) stereoisomers. The levorotatory isomer is found naturally:



Ephedrine

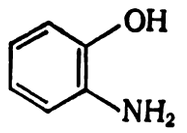


Adrenaline

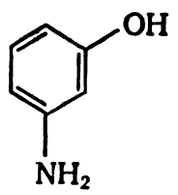
In the organism of Man and all animals, *adrenaline* acts as a hormone which controls important vital processes (carbohydrate metabolism, cardiac activity). It is similar to ephedrine structurally, but it has hydroxyl groups also in the nucleus.

Natural adrenaline is a levorotatory isomer. An interesting fact is that the physiological action of its dextrorotatory antipode is 15 times weaker.

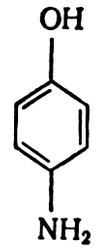
20.2. Aminophenols. These aromatic compounds are benzene derivatives and contain both the hydroxyl and the amino group in the nucleus. The simplest aminophenol has three isomers:



1,2- or *o*-Aminophenol (m.p. 174°C)



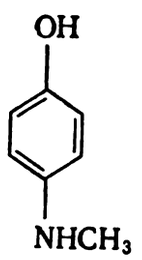
1,3- or *m*-Aminophenol (m.p. 123°C)



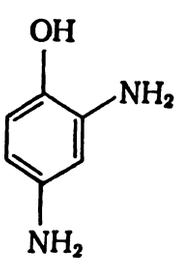
1,4- or *p*-Aminophenol (m.p. 184°C)

o- and *p*-Aminophenols are obtained by reducing the corresponding nitrophenols, which are readily produced in phenol nitration. The synthesis of *m*-aminophenol is more complicated.

Two electron-donating groups in aminophenols increase the electron density in the nucleus, and this enhances its reactivity. Aminophenols are readily oxidized, and therefore they act as reducing agents on many substances. For instance, they separate metallic silver from its salts. Owing to this property, aminophenols are used as *developers* in photography. To this end, use is made, for instance, of *metol* (4-methylaminophenol sulphate) or *amidol* (2,4-diaminophenol):

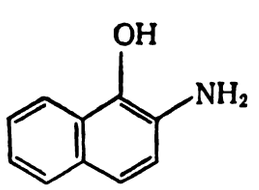


Metol

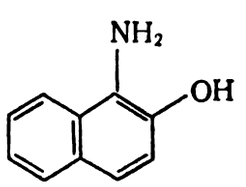


Amidol

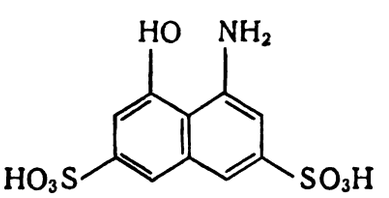
More complex compounds of this type act as intermediate products in dye synthesis. This is especially true of the naphthalene derivatives. Besides amino and hydroxyl groups, these compounds often have sulpho groups, e.g.,



2-Amino-1-naphthol

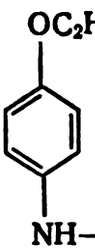


1-Amino-2-naphthol

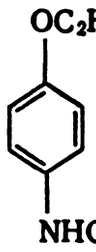


1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H acid)

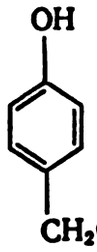
Many phenol derivatives which contain the amino group in both the nucleus and the side chain are physiologically active. They include the medicinal *phenacetin*, which is an antipyretic, *dulcin*, which is a synthetic sweet substance (it is about 500 times as sweet as sugar) and is structurally a derivative of urea, and *tyramine*, which is a poisonous substance found in the fungus ergot, a parasite on cereals (rye, wheat):



Phenacetin (1-ethoxy-4-acetyl-aminobenzene)



Dulcin (4-ethoxyphenyl urea)

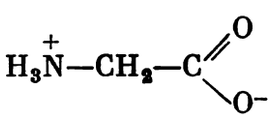


Tyramine [β-(4-hydroxy-phenyl)-ethyl-amine]

AMINO ACIDS

20.3. Physical Properties. Preparation Methods. *Amino acids* are compounds which contain the amino and carboxyl groups in the molecule. There are α-, β- and γ-amino acids, depending on the mutual arrangement of both functional groups. The simplest amino acids contain one amino group and one carboxyl group; such compounds are known as *monoaminomonocarboxylic acids*. But there are amino acids whose molecule contains two amino groups and one carboxyl group (*diaminocarboxylic acids*), one amino group and two carboxyl groups (*aminodicarboxylic acids*), etc.

The simultaneous presence of an acidic group and a basic group in a molecule of an amino acid causes intramolecular neutralization. Therefore, it would be more correct to represent free amino acids as *internal salts* of the following type:



That affects also the physical properties of amino acids: like ordinary inorganic salts, amino acids are crystalline substances which are soluble in water and sparingly soluble in organic solvents. They melt at high temperature, and usually decompose in this case. Amino acids are incapable of passing over to a vaporous state.

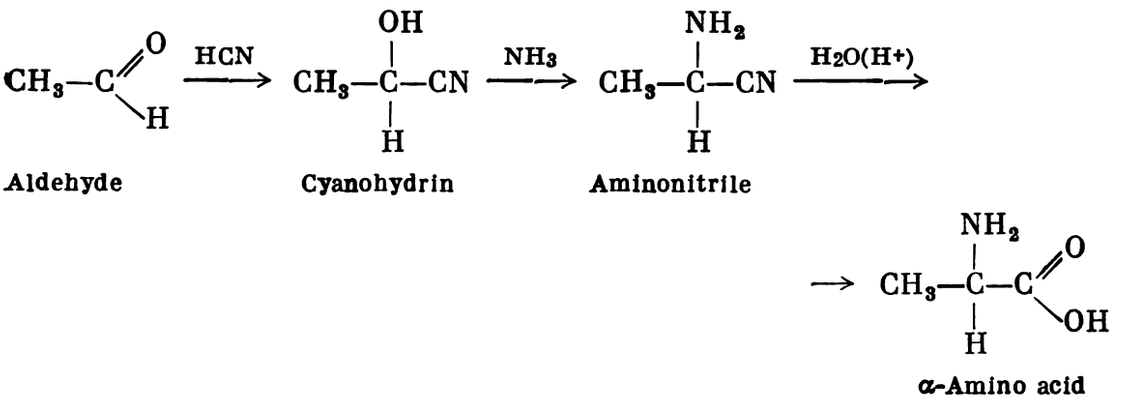
Since amino acids are important, many diverse methods of synthesizing them have been worked out:

1. The substitution of amino group for a halogen in halogen-substituted acids under the action of excess ammonia (the method had been worked out by E. Fischer at the turn of this century):

$$ClCH_2—COOH + 3NH_3 \longrightarrow H_2N—CH_2—COONH_4 + NH_4Cl$$

This method can be used to obtain amino acids of any structure from the corresponding halogen-substituted acids. In this process, the main difficulty is not in carrying out the reaction, but in separating amino acids from ammonium chloride, which is a by-product. Purification is now effected in most cases by ion-exchange resins.

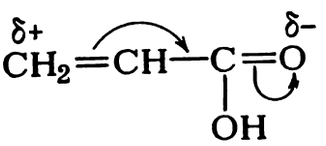
2. The action of ammonium cyanide (it acts as a mixture of hydrocyanic acid and ammonia, $NH_4CN \rightleftarrows NH_3 + HCN$) on aldehydes and ketones makes it possible to obtain α-amino acids (N. D. Zelinsky's synthesis). The process occurs through the intermediate formation of cyanohydrin, which then turns into aminonitrile that yields α-amino acid in hydrolysis:



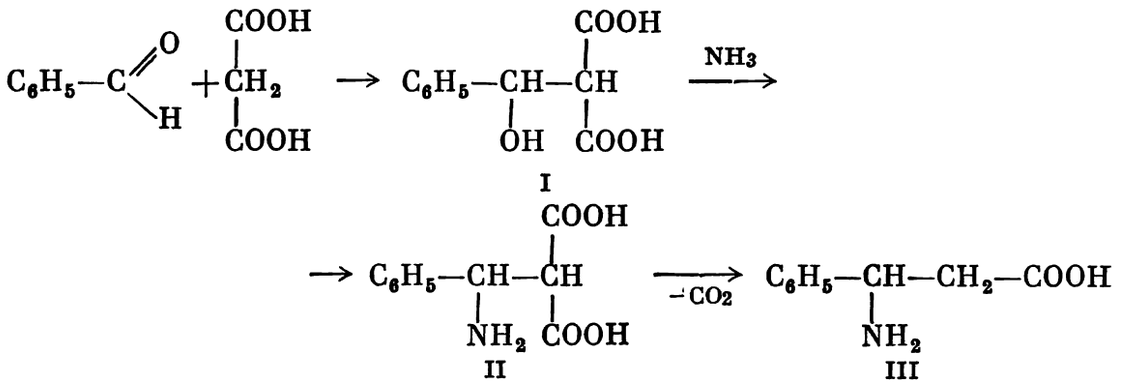
3. The addition of ammonia to α,β-unsaturated acids; in this case, β-amino acids are formed:

$$CH_2=CH—COOH \xrightarrow{NH_3} H_2N—CH_2—CH_2—COOH$$

Such an order of addition (contrary to Markovnikov's rule) is predetermined by the polarization of the double bond under the influence of the carboxyl group:

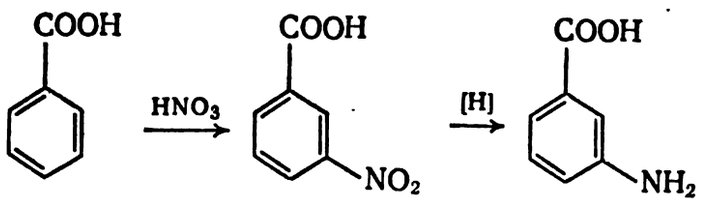


4. The action of aldehydes and ammonia on malonic acid (β-amino acid synthesis by V. M. Rodionov's method):



Condensation of the aldol type occurs at the first stage of this reaction; in it, malonic acid with its mobile hydrogen atoms of the CH_2 group acts as a methylene component. In the condensation product I, the hydroxyl group is replaced by the amino group under the action of ammonia (compare synthesis of α-amino acids by Zelinsky's method), and the intermediate product II is subjected to decarboxylation.

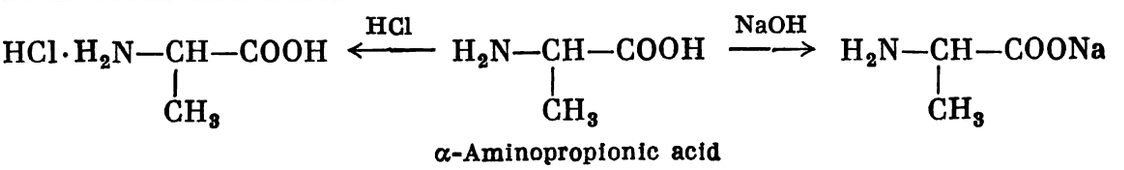
5. Reduction of nitro-substituted acids. This method is of the greatest importance in the synthesis of aromatic amino acids:



The given methods are only some of the proposed ways of synthesizing amino acids.

20.4. Chemical Properties. Like in other heterofunctional compounds, the properties of amino acids in the first approximation are the sum of the properties of the functions which are in their composition.

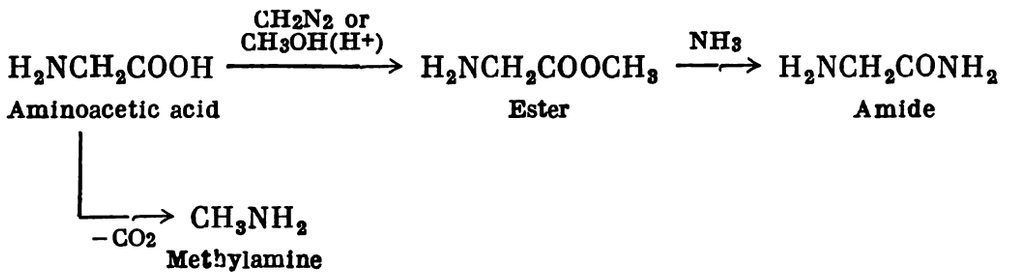
Amino acids are peculiar especially because they have two functions of an opposite chemical nature, i.e., an amino group with basic properties and a carboxyl group with acidic properties. Amino acids, like such inorganic substances as hydroxides of aluminium and zinc, are *amphoteric* compounds which possess both acidic and basic properties. Since amino acids are amphoteric, they can form salts with both acids and bases:



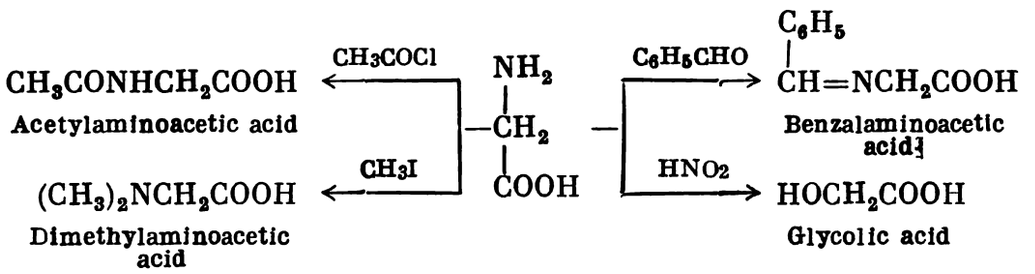
α-Aminopropionic acid

Either of the functional groups of amino acids can participate also in other reactions of these acids. These reactions are similar to those of amines and acids, and therefore there is no need to deal with them at length; let us consider only several typical reactions carried out with aminoacetic acid (glycine).

Reactions at the carboxyl group:

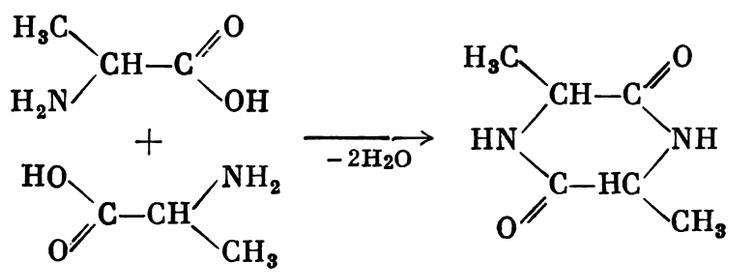


Reactions at the amino group:

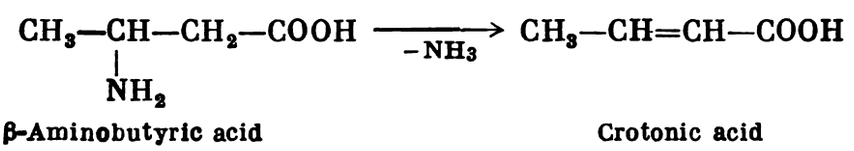


The properties of amino acids, like those of other heterofunctional compounds, depend on the mutual arrangement of the amino group and the carboxyl.

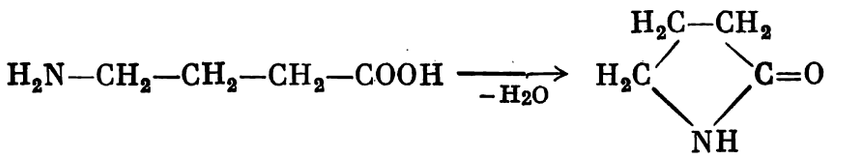
On heating, α-amino acids form cyclic amides made out of two molecules of α-amino acids. Such compounds are known as *diketopiperazines*:



Beta amino acids lose the ammonia molecule more readily than others and turn into unsaturated acids:



Gamma amino acids form intramolecular cyclic amides known as *lactams*:



γ-Aminobutyric acid — γ-Aminobutyric lactam

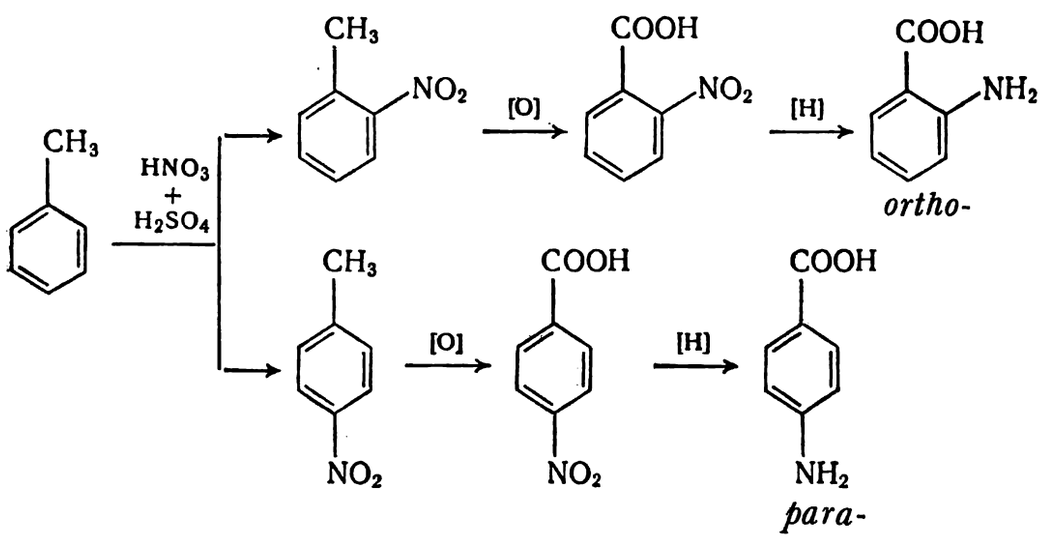
There is a certain similarity between α-, β- and γ-amino acids and the respective hydroxy acids in their behaviour toward heating (see Sec. 18.2).

20.5. Important Individual Amino Acids. The most important amino acids are α-amino acids, which form monomeric units of protein molecules (see Sec. 22.2). These acids will be dealt with at greater length in the chapter on proteins. Here, let us consider only the simplest α-amino acid: *α-aminoacetic acid*, $H_2N—CH_2—COOH$. It is known also as *glycocoll* or *glycine*.

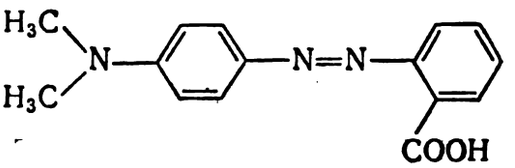
Like all amino acids, glycocoll is a colourless crystalline substance which dissolves in water. It is obtained by synthesis from chloroacetic acid and ammonia.

Amino acids, which contain functions in the benzene or naphthalene nucleus, are important as intermediate products in the synthesis of dyes and medicinals.

Aminobenzoic Acids. Among the three isomeric acids, *o*-aminobenzoic (*anthranilic*) and *p*-aminobenzoic acids are of the greatest importance. The starting material for their synthesis is toluene, which is turned into a mixture of *o*- and *p*-nitrotoluenes by nitration and then into *o*- and *p*-nitrobenzoic acids by oxidation; when these acids are reduced, aminobenzoic acids are obtained:

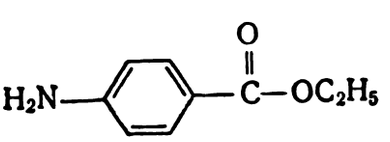


Anthranilic acid (*ortho*-isomer) is used in dye synthesis. For example, the azo dye called methyl red is obtained after diazotization and azo coupling with dimethylaniline:

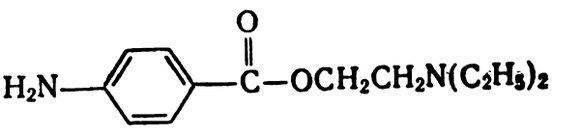


This substance is used as an indicator: it is red in an acid medium, and yellow in an alkaline one.

The derivatives of *p*-aminobenzoic acid include important medicinals:



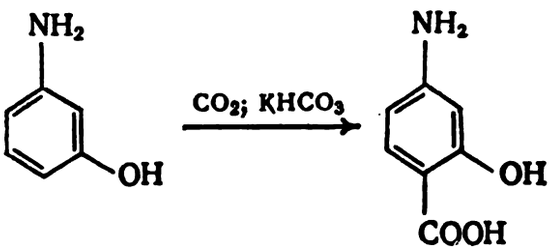
Anesthesin (ethyl *p*-aminobenzoate)



Novocain (diethylaminoethyl-*p*-aminobenzoate)

Both substances are local anesthetics. They are a substitute for cocaine, a natural alkaloid which is dangerous to use because one becomes addicted to it.

p-Aminosalicylic acid (PAS) has become important as a medicinal for treating tuberculosis. It is prepared from *m*-aminophenol and carbon dioxide (the reaction is similar to salicylic-acid synthesis, see Sec. 18.4):



PART IV
HETEROCYCLIC COMPOUNDS

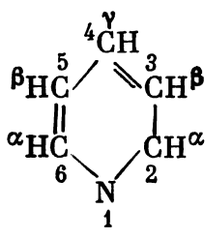
Chapter 21
SIX-MEMBERED AND FIVE-MEMBERED HETEROCYCLES. ALKALOIDS

Heterocyclic compounds are those in which an element other than carbon (*a heteroatom*) is contained in a ring.

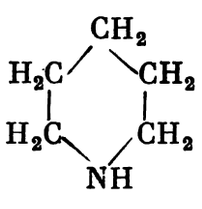
21.1. Classification and General Characteristics. Heterocyclic compounds are classified by the nature of the heteroatom, and then they are subdivided according to the number of heteroatoms, the number of units in a ring, and other signs.

The most important heterocyclic compounds are those in which the N, O or S atoms are in the composition of six- and five-membered rings. These compounds can structurally be analogues of cycloparaffins, but unsaturated heterocyclic compounds, being analogues of aromatic compounds, are more important.

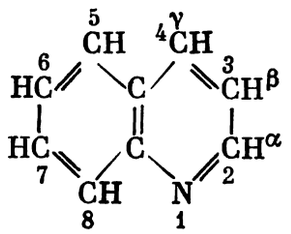
The formulas and names of the most important heterocyclic rings are given below. The formulas show that numeration always begins with the heteroatom. Another technique is also used for simple compounds, i.e., atoms are denoted by Greek letters: atoms which are nearest to the heteroatom are denoted by α, and those coming next by β and γ:



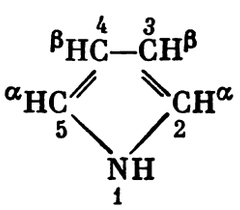
Pyridine



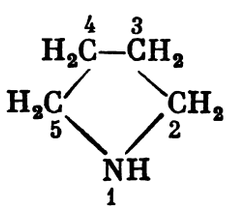
Piperidine



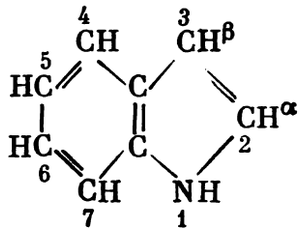
Quinoline



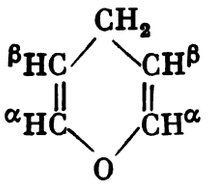
Pyrrole



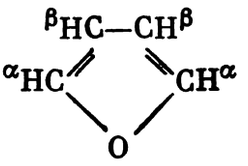
Pyrrolidine



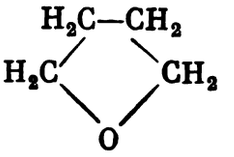
Indole



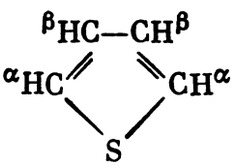
Pyran



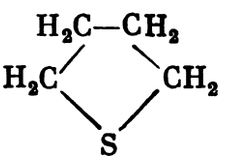
Furan



Tetrahydrofuran

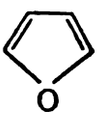


Thiophene

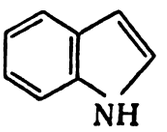


Thiophane

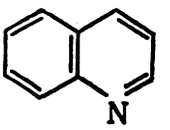
Heterocyclic rings are usually represented not by complete formulas, but by conventional schemes, as is done for aromatic compounds:



Furan



Indole



Quinoline

Heterocyclic compounds, like hydrocarbons, are the basis for obtaining many various derivatives which have different substituents in molecules. For instance, there are heterocyclic halogen- and hydroxyderivatives, aldehydes, ketones, carboxylic and sulphonic acids, nitro compounds, amines, etc. The properties of the corresponding heterocyclic compounds are, in general, similar to those of analogous noncyclic or carbocyclic compounds. Thus, it is considerably easier to study heterocyclic compounds, because this study is largely a repetition of what has been learned. In our exposition, attention will be drawn more to the difference in properties than to their similarity.

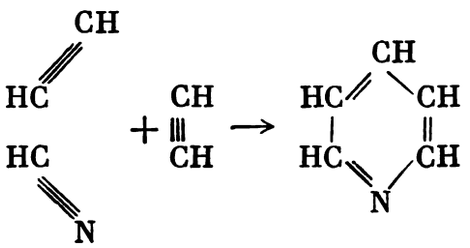
Heterocyclic compounds are peculiar because of their nucleus, whose features often largely determine the properties of a compound as a whole.

The chemistry of heterocyclic compounds is now rapidly developing, because this class of compounds includes important natural substances, several valuable medicinals, dyes, and other practically important substances. Voluminous works on heterocyclic compounds have been written; in this book, we can only briefly discuss the fundamentals of this extensive field.

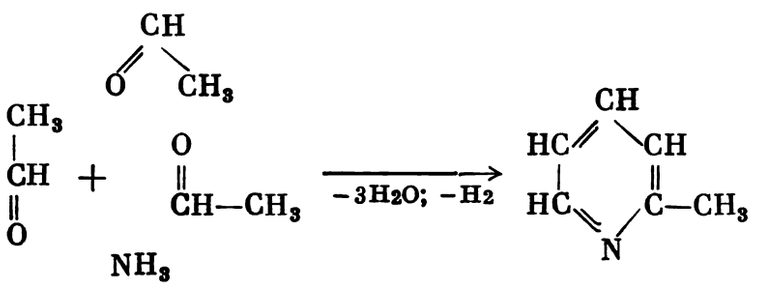
SIX-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

21.2. Pyridine and Its Derivatives. Pyridine can be regarded as a nitrogen analogue of benzene. This liquid (b.p. 115°C) has a peculiar unpleasant odour, and mixes with water in all proportions. Pyridine and its immediate homologues are contained in coal tar, which is their industrial source. They can be obtained synthetically as well.

The pyridine structure can be seen most clearly from a synthesis in which acetylene and hydrocyanic acid are the starting materials:



According to A.E. Chichibabin, pyridine homologues can be obtained by condensing aldehydes with ammonia (this synthesis is important industrially). For instance, α-methylpyridine is obtained from acetaldehyde:

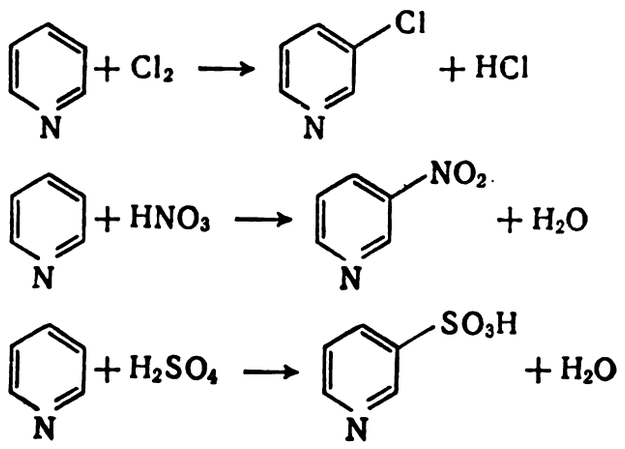


α-Methylpyridine (α-picoline)

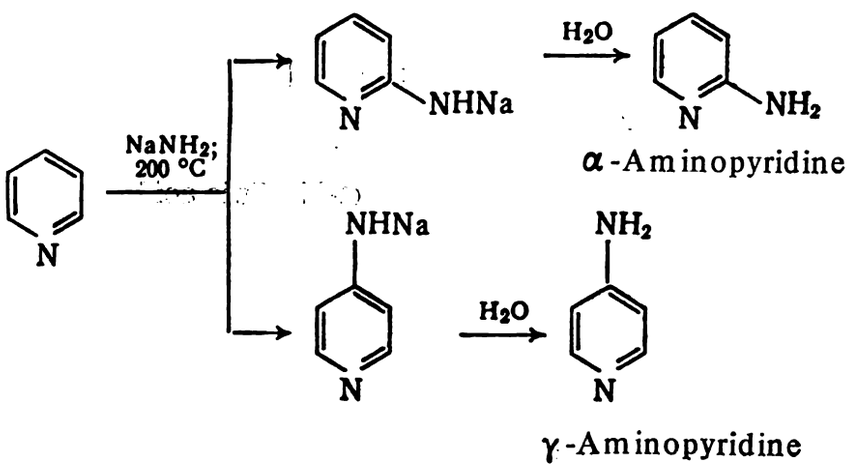
Pyridine, like amines, possesses *basic* properties due to the free electron pair, which is attached to the nitrogen atom. But pyridine is a weaker base than aliphatic amines, because the free electron pair of pyridine nitrogen is conjugated with the π-electron system of the pyridine ring.

Chemical properties. Owing to the presence of the aromatic sextet, the properties of the pyridine ring are similar to those of benzene in many respects. Pyridine, like benzene, is characterized by *electrophilic substitution* reactions. It undergoes halogenation, nitration and sulphonation. In this case, the nitrogen atom of the pyridine ring acts as a meta-orienting substituent which directs the entering groups toward the *meta*-position and hinders (in comparison with

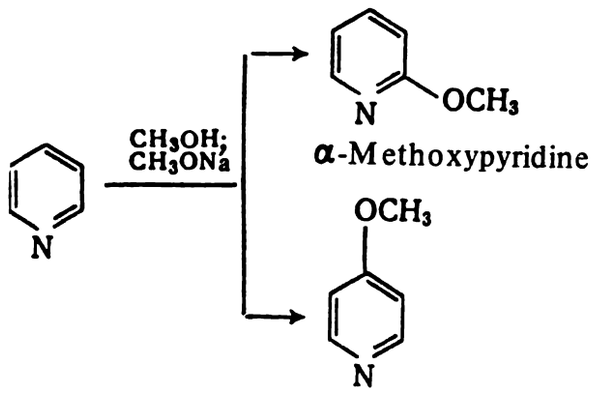
benzene) electrophilic substitution reactions:



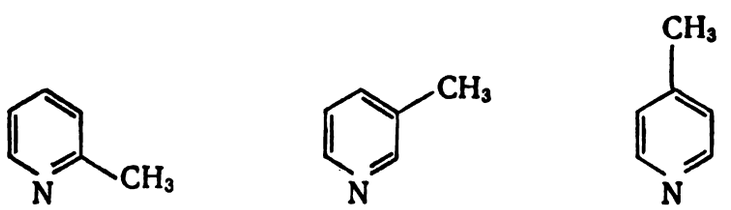
The nitrogen atom thus affects the properties of the pyridine ring, because nitrogen, being a more electronegative element than carbon, draws the electron density of the ring toward itself. Whenever the mesomeric effect is exhibited in aromatic systems, it is transmitted mainly in the *ortho*- and *para*-positions, i.e., it is transmitted to the atoms 2, 4 and 6, which become *depleted* of electrons (like *ortho*- and *para*-positions in nitrobenzene). The electron density of the atoms 3 and 5 is somewhat greater, and therefore electrophilic substitution reactions are directed toward them. But the atoms 2, 4 and 6 (α- and γ-positions) become capable of entering into *nucleophilic substitution* reactions, because they are depleted of electrons. One such transformation is direct pyridine amination (*Chichibabin's reaction*) which is effected by sodium amide or potassium amide in an inert hydrocarbon solvent (kerosene, xylene) on heating:



A similar nucleophilic substitution reaction occurs also when sodium methoxide acts on pyridine:

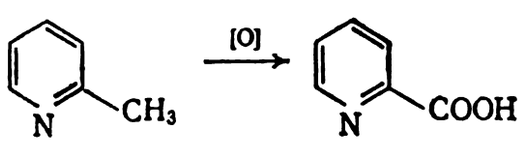


Monosubstituted homologues of pyridine can exist as three isomers which are similar to the *ortho-*, *meta-* and *para-*isomers in the benzene series. This is true of methyl-substituted pyridines called *picolines*:



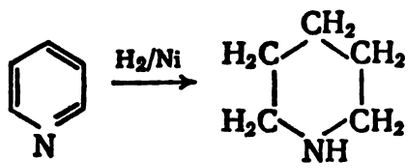
α-Methylpyridine (α-picoline) | β-Methylpyridine (β-picoline) | γ-Methylpyridine (γ-picoline)

When *oxidizing agents* act on pyridine homologues, they behave similarly as hydrocarbons of the benzene series, i.e., only the side chain of the compound is affected, and it becomes a carboxyl group (the oxidizing agent in this case is a chromic-acid mixture):

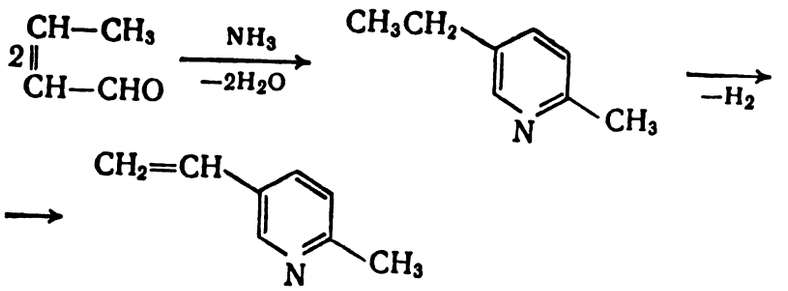


α-Picoline — α-Picolinic acid

In catalytic hydrogenation, pyridine is converted into *piperidine*, whose structure and properties are those of a secondary amine:



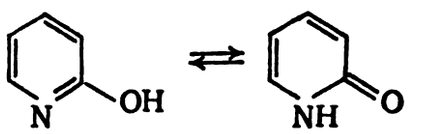
Among pyridine homologues, 2-methyl-5-vinylpyridine is of great importance; it is obtained from ammonia and crotonaldehyde:



Various substituents, i.e., halogens and hydroxy, nitro, sulpho and amino groups, can be introduced into the pyridine ring. In this case, the properties of the corresponding compounds greatly depend on the position of the substituent in the pyridine ring. As a rule, β-substituted pyridines are the most similar to the respective aromatic compounds. For example, the halogen atom in *β-chloropyridine* is characterized by low reactivity, and this is also true of chlorobenzene.

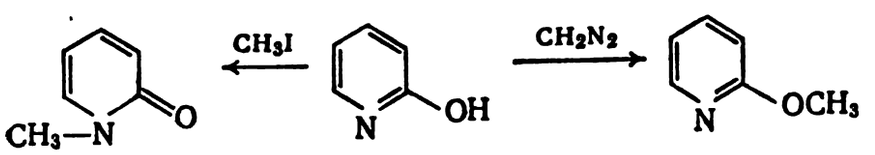
Other properties are inherent in α- and γ-derivatives of pyridine. In α- and γ-chloropyridines, the halogen atom is more mobile, as is the case with *o*- and *p*-nitrochlorobenzenes. This becomes clear if it is recalled that the mesomeric effect transmits the influence of the substituent in the *ortho*- and *para*-positions of the aromatic series. For pyridine, they are α- and γ-positions, respectively; they are under the influence of the ring nitrogen which acts as a *meta*-director.

Peculiar properties are possessed by α- and γ-amino- or hydroxypyridines, which act as tautomeric substances, e.g.,



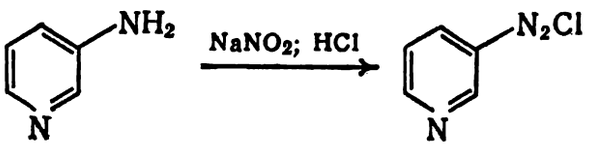
α-Hydroxypyridine α-Pyridone

This is proven by the fact that the derivatives of both the hydroxypyridine and pyridine forms are obtained in chemical transformations:



N-Methyl-2-pyridone 2-Hydroxypyridine 2-Methoxypyridine

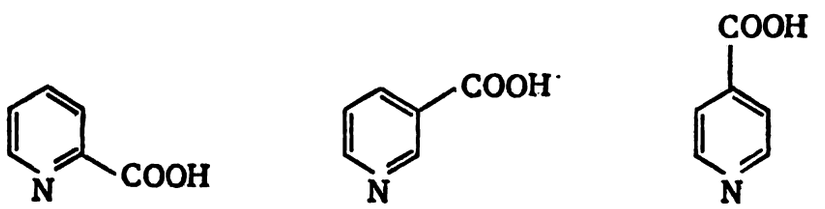
Similar behaviour is exhibited by γ-hydroxypyridine, as well as by α- and γ-aminopyridines. Alpha and gamma aminopyridines differ from ordinary aromatic amines also in that they are incapable of turning into diazo compounds. Beta aminopyridine is diazotized normally:



Pyridine-β-diazonium chloride

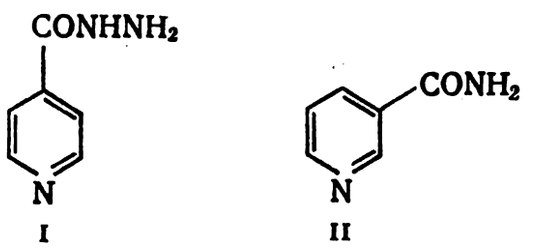
The diazo compound obtained enters into reactions with the loss of nitrogen, which are usual for aromatic diazo compounds, and also into azo coupling reactions.

Pyridinecarboxylic acids have been studied well:



α-Pyridine-carboxylic (picolinic) | β-Pyridine-carboxylic (nicotinic) | γ-Pyridine-carboxylic (isonicotinic)

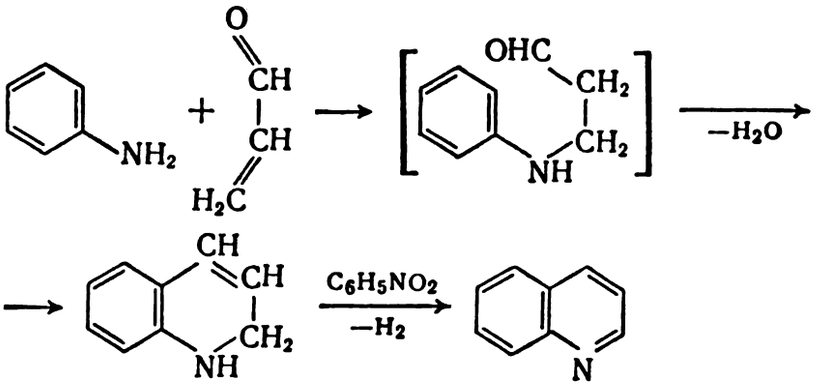
Isonicotinic acid hydrazide I, known as *isoniazid*, is used as a medicinal for treating tuberculosis. Nicotinamide II (vitamin PP) is a substance whose deficiency causes the disease called pellagra.



I II

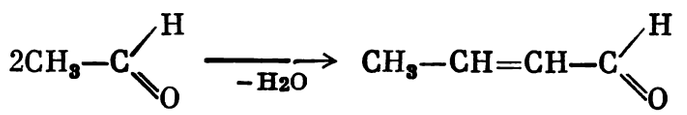
21.3. Quinoline and Its Derivatives. Quinoline is a heterocyclic analogue of naphthalene. It is contained in coal tar, but it can be obtained by *Skraup synthesis*, i.e., by heating a mixture of aniline, nitrobenzene, glycerol and sulphuric acid. Glycerol is dehydrated under the action of sulphuric acid and acrolein is formed (see Sec. 11.6). Acrolein is added to aniline, and then the aldehyde formed is condensed. Moreover, water is eliminated and dihydroquino-

line is formed; dihydroquinoline becomes quinoline under the action of nitrobenzene (which acts as an oxidizing agent):

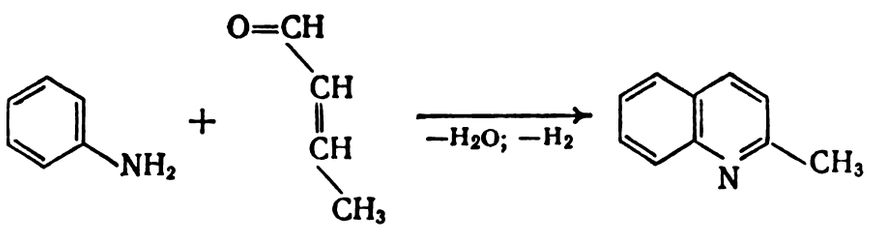


Dihydroquinoline Quinoline

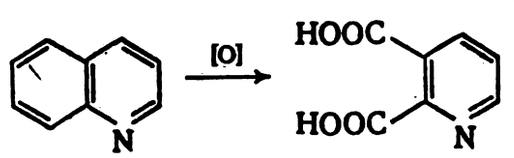
Quinoline homologues can be obtained by the *Döbner-Miller synthesis*, which differs from the Skraup synthesis in that α,β-unsaturated aldehyde is obtained in the course of a reaction by croton condensation. For example, *α-methylquinoline* (*quinaldine*) is obtained from aniline and acetaldehyde:



Crotonaldehyde



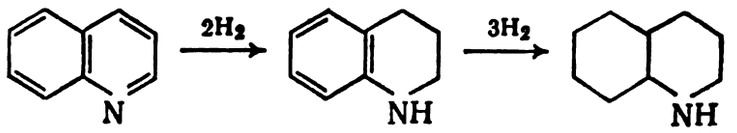
Quinoline is an oily liquid with an unpleasant odour, which dissolves sparingly in water. It has some chemical properties in common with pyridine: it is also a base and enters into the same reactions as pyridine. In quinoline, however, *electrophilic substitution* is directed mainly to the *benzene ring*, and this clearly shows that the pyridine nucleus is less reactive than the benzene one. This is exhibited also in quinoline oxidation, in which the benzene ring is destroyed:



Quinoline Quinolinic acid

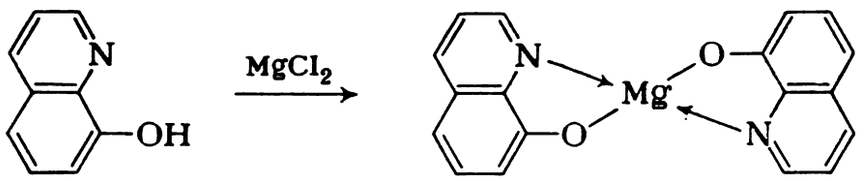
In nucleophilic substitution reactions, the substituent enters into the pyridine ring.

In *hydrogenation*, quinoline, like pyridine, turns into the corresponding saturated compounds which, by their chemical properties, do not differ from ordinary aliphatic amines:

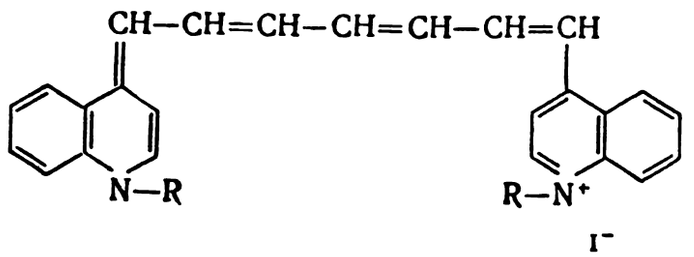


Tetrahydroquinoline — Decahydroquinoline

8-Hydroxyquinoline (crystalline substance, m.p. 75°C) is widely used as a reagent for ions of many metals with which it forms chelates:



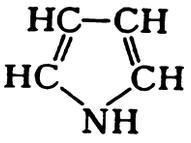
Quinoline derivatives, *cyanine dyes*, are used as *sensitizers*, i.e., substances which make photographic materials sensitive to longer-wavelength irradiation (yellow, red, and infrared parts of the spectrum). A representative of such a type of dyes is *xenocyanin*:



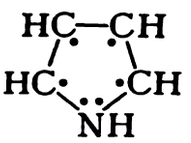
FIVE-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

21.4. Structure and General Properties. The simplest five-membered heterocycles are pyrrole, furan and thiophene. They all exhibit aromatic properties. They are aromatic for the same reason as benzene, i.e., a sextet of mobile electrons is present in them, but the formation of the sextet is different. Each carbon atom introduces an electron into the sextet, while the free electron pair of the heteroatom introduces another two electrons into it. For example, the structure

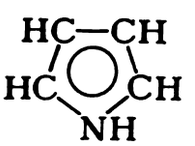
of pyrrole I can be schematically illustrated by formulas II and III:



I



II

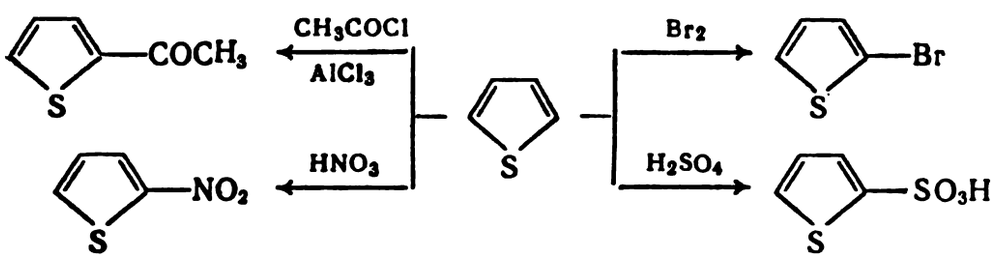


III

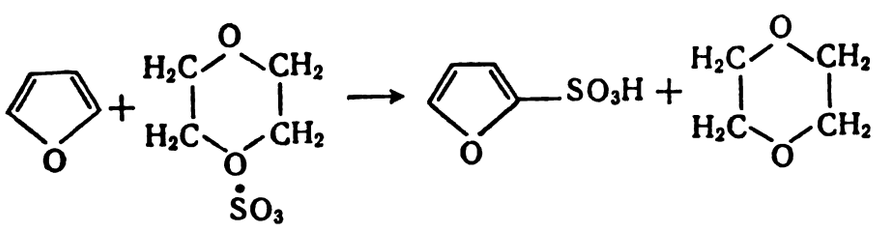
The electron pair of pyrrole nitrogen no longer has the properties of a free electron pair, which determines the basicity of amines and pyridine, but participates in the formation of the electron sextet. Therefore, pyrrole nitrogen has almost no basic properties.

Nevertheless, an electron pair of nitrogen is extended from the sextet under the action of strong mineral acids, and pyrrole, having lost its aromaticity, becomes an unstable unsaturated compound which is immediately polymerized. This is how the resinification of pyrrole is explained when strong mineral acids act on it. Furan acts similarly. Thiophene is not degraded by acids.

The aromatic properties of five-membered heterocyclic compounds are exhibited in their ability to undergo electrophilic substitution reactions, i.e., halogenation, nitration, sulphonation, alkylation and acylation according to the Friedel-Crafts method. These reactions can be carried out most simply with thiophene, because it is not degraded under the action of acids:

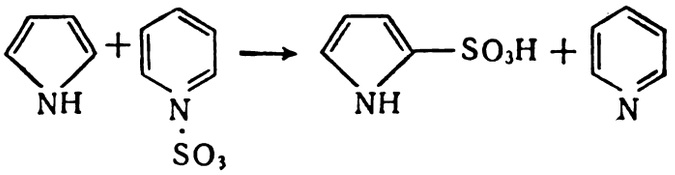


But things are more complicated when furan and pyrrole are involved, because they are destructed under the action of acids. Therefore, in sulphonation, for example, sulphuric anhydride, which is bound into a complex compound with dioxane (reaction 1) or pyridine (reaction 2), is used as a reagent (A. P. Terentyev):



(1)

Furan — Dioxane sulphotrioxide — Furan-α-sulphonic acid — Dioxane

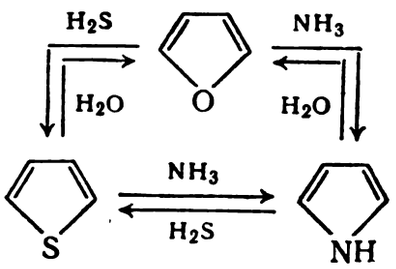


(2)

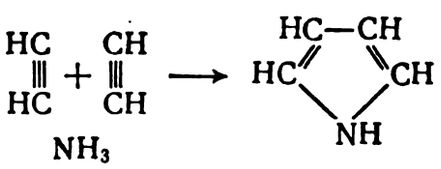
Pyrrole | Pyridine-sulpho-trioxide | Pyrrole-α-sulphonic acid | Pyridine

The foregoing examples show that the substituents enter mainly into the α-position of five-membered heterocycles.

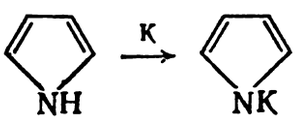
The relationship of the five-membered heterocyclic compounds of pyrrole, furan and thiophene is expressed in their interconversions over the catalyst Al_2O_3 at 400-450°C in a current of H_2S, NH_3 and H_2O, respectively (*Yu. K. Yuryev's reaction*):



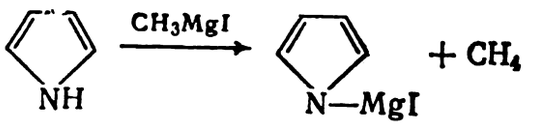
21.5. Pyrrole and Its Derivatives. Pyrrole is obtained from furan by means of Yuryev's reaction or by condensing acetylene with ammonia according to the following scheme:



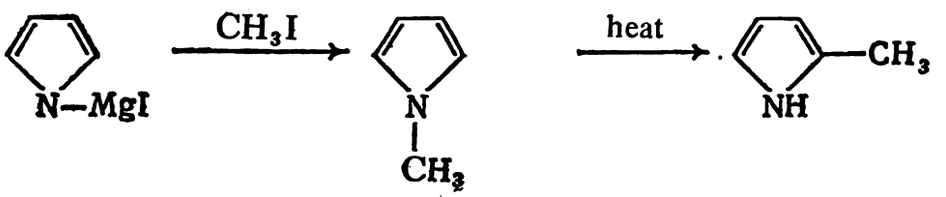
It is a colourless mobile liquid which boils at 130°C. In air, it is rapidly oxidized and darkens. To detect pyrrole, use is often made of its ability to redden a pine chip which is wetted with hydrochloric acid. Besides the given general properties, pyrrole exhibits the properties of a very weak acid. This is revealed by the ability of the hydrogen, which is attached to the nitrogen atom, to be replaced by a metal, for instance, under the action of potassium:



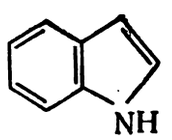
A similar reaction occurs under the action of organomagnesium compounds:



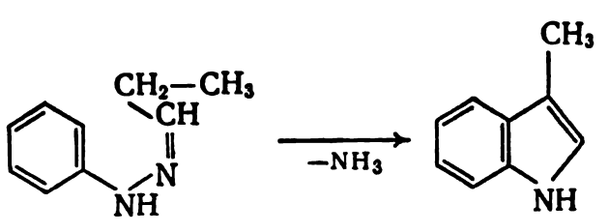
N-pyrryl potassium and N-pyrryl magnesium halides give N-alkyl derivatives of pyrrole under the action of alkyl halides; these derivatives are rearranged into C-alkyl derivatives on heating, e.g.,



Indole is a condensed bicyclic system which consists of benzene and pyrrole rings:



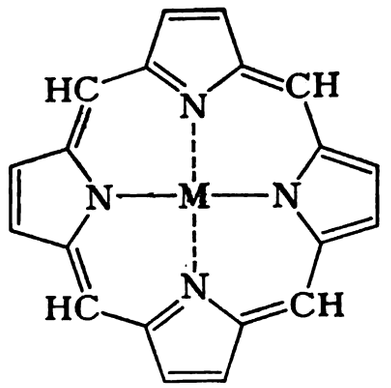
There are many ways of obtaining compounds of the indole series. One of the most important ways is by *Fischer's indole synthesis.* The starting materials are phenylhydrazones of aldehydes and ketones, which are heated together with $ZnCl_2$ or $CuCl_2$:



Phenylhydrazone of propionaldehyde — β-Methylindole (skatole)

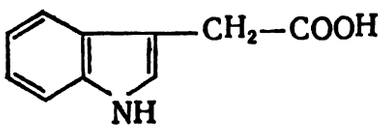
Compounds of the pyrrole and indole series are often found naturally. Many synthetic preparations of the pyrrole and indole series are very active physiologically, and they are used as medicinals, growth stimulants, etc. For instance, pyrrole rings are in the composition of the most important natural substances: *chlorophyll* and *hemoglobin.* Both compounds are based on the structure made out of

four pyrrole rings, which can be schematically illustrated as follows:



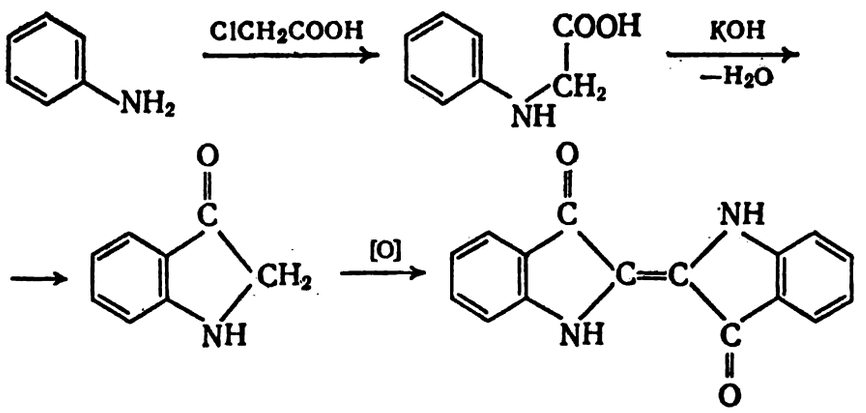
The scheme does not show the side chains of the molecule. Metal which is linked with pyrrole atoms of nitrogen, i.e., magnesium in chlorophyll and iron in hemoglobin, is in the centre. The entire structure is connected also with the protein part, without which neither chlorophyll nor hemoglobin can perform their biochemical functions.

Indolylacetic acid (*heteroauxin*) is capable of stimulating plant growth and promoting grafting. It has the following structure:



An important protein amino acid, *tryptophan* (see Sec. 22.1), is an indole derivative.

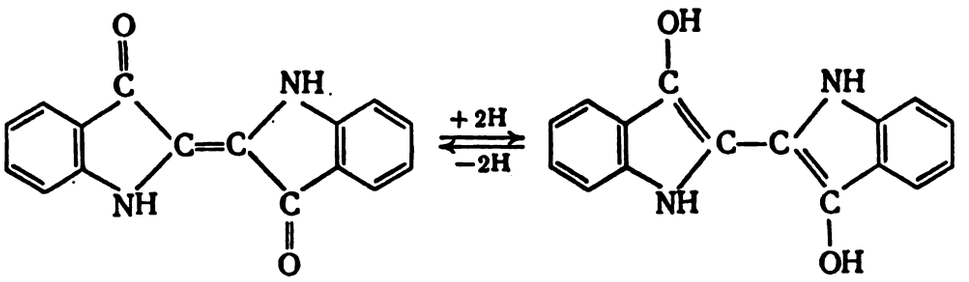
The *indigo dye* is also an indole derivative. It was extracted from plants for many centuries. In the nineteenth century, Baeyer ascertained the formula for indigo after many years' research work. Later, its industrial synthesis was mastered. One of the syntheses is based on aniline and chloroacetic acid:



Indoxyl Indigo

Cloth cannot be directly dyed by indigo, because the dye is insoluble in water. Therefore, indigo is reduced to colourless *white indigo*

under the action of weak reducing agents in an alkaline medium. Cloth is then impregnated with this solution, and indigo is formed on it after oxidation by atmospheric oxygen:



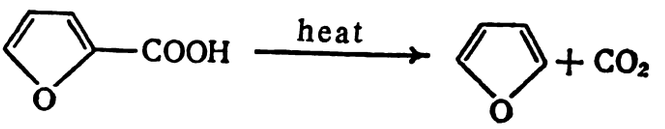
Indigo White indigo

Such a method of dyeing is known as *vat dyeing*.

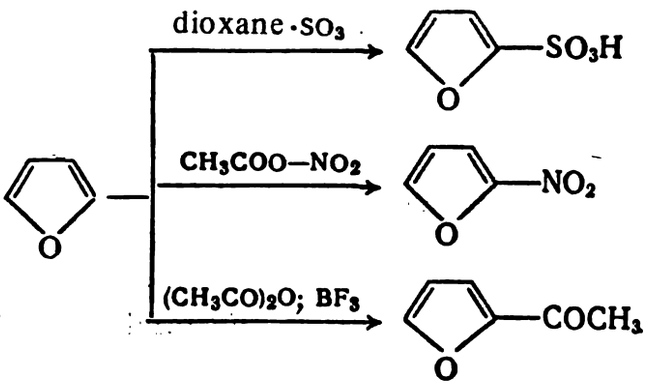
The production of indigo was one of the first achievements in industrial organic synthesis in the nineteenth century. Synthetic indigo is being produced even now, but it has lost its title of "king of dyes", because other fast dyes producing beautiful colours have been obtained.

The principle used in dyeing by means of indigo is also employed in dyeing by means of modern vat dyes.

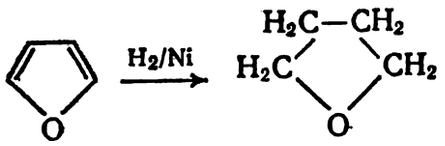
21.6. Furan and Its Derivatives. Furan is obtained by decarboxylating pyromucic acid:



It is a colourless, mobile, low-boiling liquid (b.p. 31°C), which is oxidized in air and darkens. Furan is readily destructed by acids. Therefore, electrophilic substitution reactions in the furan series are carried out in such a way as to protect furan from the destructive action of acids, i.e., dioxane sulphotrioxide is used in sulphonation, acetyl nitrate, in nitration, and the boron trifluoride catalyst is used instead of the more active aluminium chloride in acylation:



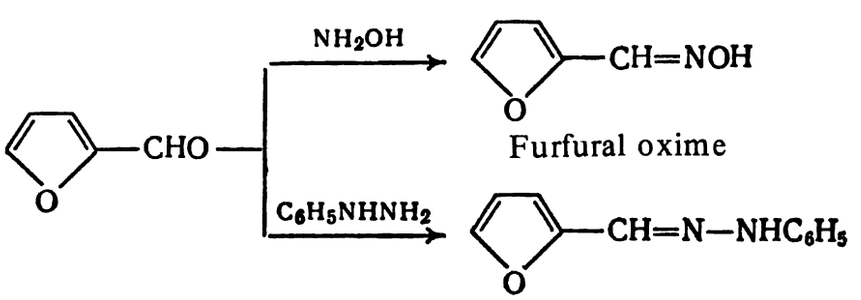
Electrophilic substitution reactions occur readily in the furan ring; furan is similar to phenol by its reactivity. Nitric acid oxidizes furan with ring degradation. Tetrahydrofuran is obtained in catalytic hydrogenation:



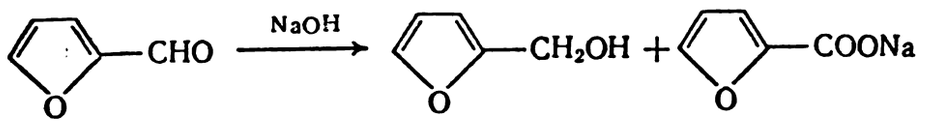
Tetrahydrofuran is an intramolecular ether of 1,4-butanediol. Like all other ethers, it is rather inert chemically. It is used as a good solvent.

The most easily available compound of the furan series, the aldehyde called *furfural*, is formed when pentoses with dilute acids are heated (see Sec. 19.3). The source of pentoses are the polysaccharides called *pentosans*, which are contained in large amounts in various products of plant origin, such as siftings, sunflower husk and corncobs. Large amounts of furfural are obtained when these and other agricultural wastes are processed industrially. It is used for producing polymeric materials, as a solvent in some oil-refining processes and as starting material for synthesizing other compounds of the furan series.

Furfural is a colourless liquid which boils at 161°C. Bread has its peculiar odour because of the presence of traces of furfural, which is formed from pentoses in flour when bread is being baked. Furfural is rapidly oxidized in air, turning at first into a brown liquid, and then into a black resin. It has all the properties of an aldehyde, i.e., its oxime, phenylhydrazone and other derivatives can be obtained:



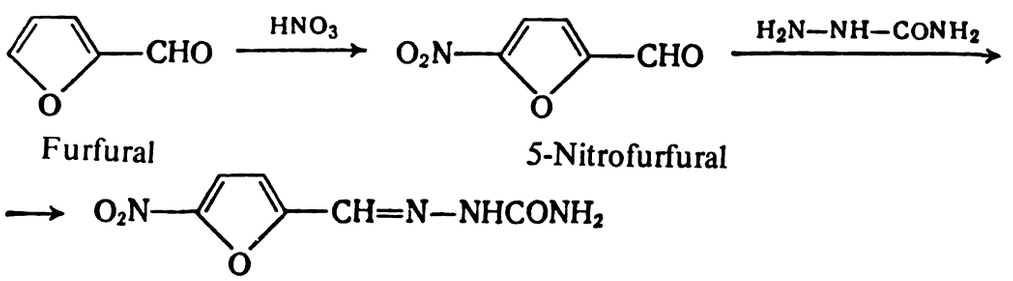
It can enter into the Cannizzaro reaction:



Furyl alcohol Sodium pyromucate

Furyl alcohol is formed when furfural is reduced, and pyromucic acid is formed when it is oxidized.

Aromatic properties of the furan ring in furfural are exhibited in its ability to enter into electrophilic substitution reactions. For instance, 5-nitrofurfural and then its semicarbazone were obtained by nitrating furfural:

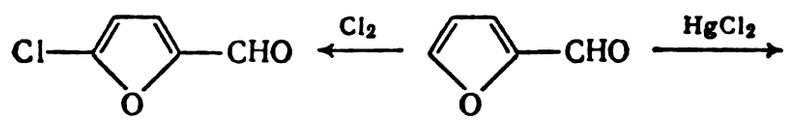


Furfural 5-Nitrofurfural

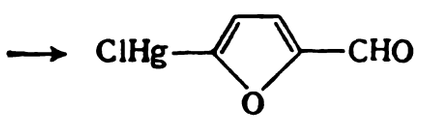
5-Nitrofurfural semicarbazone
(Furacilin)

5-Nitrofurfural semicarbazone called *Furacilin* (yellow crystals, m.p. 227-232°C) is used as an external disinfectant and is taken orally as medicine for treating dysentery.

Other examples of electrophilic substitution reactions are the chlorination and mercuration of furfural:



5-Chlorofurfural

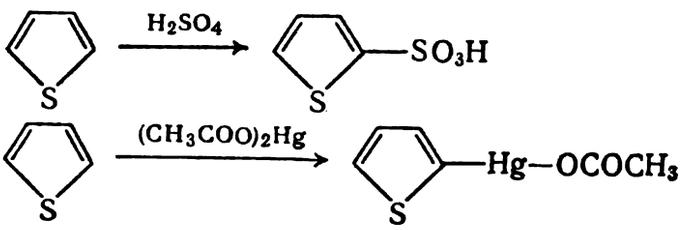


5-Chloromercurofurfural

21.7. Thiophene and Its Derivatives. Thiophene is the most stable heterocyclic compound among the five-membered heterocyclic compounds which we have considered. It is stable in air, and is not destructed by acids. It is a typical aromatic compound: it can be chlo-

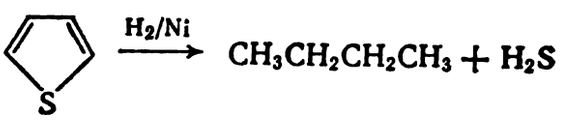
rinated and nitrated, and ketones can be obtained from it by the Friedel-Crafts reaction.

The boiling point of thiophene is very close to that of benzene (84°C and 80°C, respectively), and therefore it is difficult to separate them from one another by distillation. Thiophene can be removed from benzene only chemically by taking advantage of the fact that the former enters into sulphonation and mercuration reactions more readily than the latter:



The discovery of thiophene is interesting. The famous German chemist Victor Meyer was demonstrating, at his lectures, a colour reaction which was considered to be characteristic of benzene. But once the reaction did not occur. In trying to find out why the experiment failed, Meyer ascertained that the colour reaction was produced only by benzene which was separated from coal tar, while benzene obtained by decarboxylating benzoic acid did not produce it. Therefore, he concluded that benzene of coal origin contains an impurity which produces the colouring. Meyer then succeeded in isolating a sulphur-containing substance, which he called thiophene.

Compounds of the thiophene series are contained in large amounts in some types of petroleum. The presence of sulphur compounds in petroleum is highly undesirable: if they are not removed in the course of refining, sulphur dioxide, which causes great corrosion, is formed when fuel is consumed. Therefore, petroleum is subjected to *desulphuration*. One of the methods is based on N. D. Zelinsky's works and consists in the catalytic hydrogenation (250°C, 50 kg/cm^2) of thiophene compounds with the isolation of sulphur in the form of hydrogen sulphide:

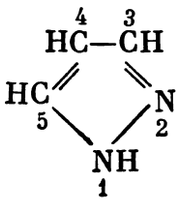


The content of sulphur compounds in petroleum can reach tens of per cent, and therefore it is important to find ways of putting them to good use instead of destroying them. Such methods are now being intensively worked out.

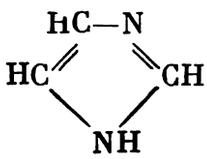
COMPLEX HETEROCYCLIC COMPOUNDS AND ALKALOIDS

21.8. Heterocycles with Several Heteroatoms. These heterocyclic compounds include important natural substances, and they are used to obtain medicinals, dyes and other products of organic synthesis. The most important heterocyclic compounds of this type contain either several nitrogen atoms or nitrogen in combination with other heteroatoms.

Pyrazole and *imidazole* are five-membered heterocyclic compounds with two nitrogen atoms. They are isomers which differ by the arrangement of heteroatoms:

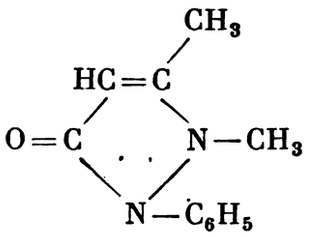


Pyrazole

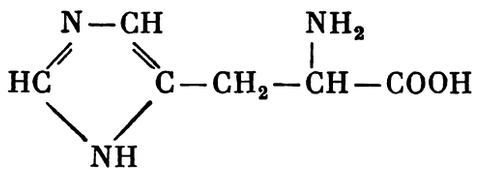


Imidazole

Both heterocyclic compounds are crystalline substances (m.p. 70°C and 90°C, respectively) which have properties of weak bases and are aromatic. For instance, pyrazole is very stable toward the action of oxidizing agents, and it enters into electrophilic substitution reactions (nitration, sulphonation, and bromination). Important derivatives of these heterocycles are *antipyrine*, which is an antipyretic and analgesic, and *histidine*, which is a protein amino acid:

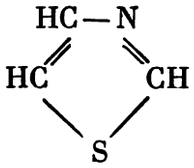


Antipyrine

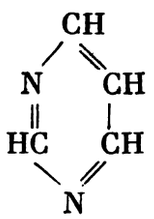


Histidine

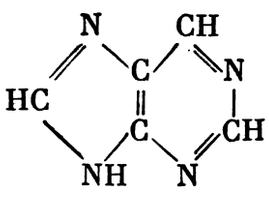
Thiazole is a liquid which boils at 117°C. It dissolves in water, and possesses properties of a weak base. The thiazole ring is contained in the molecule of vitamin B_1, the antibiotic called penicillin, and the sulphamide drug called sulphathiazole:



Thiazole

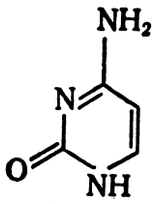


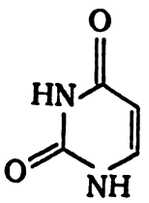
Pyrimidine

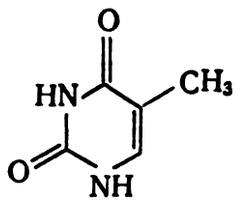


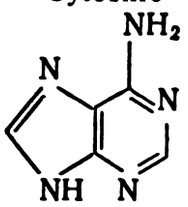
Purine

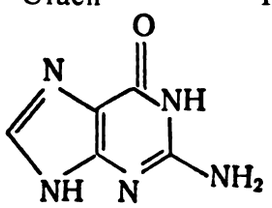
Compounds which are the derivatives of *pyrimidine* and *purine* are important naturally:


Cytosine


Uracil


Thymine


Adenine

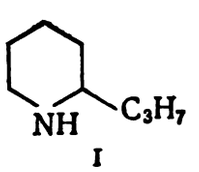

Guanine

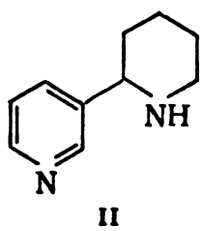
These substances, being pyrimidine and purine bases, are in the composition of *nucleic acids*, which are of great importance naturally (see Sec. 22.4).

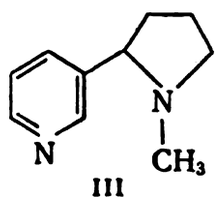
21.9. Alkaloids. Alkaloids are organic nitrogen bases (usually heterocyclic) in plants. For animals and Man, alkaloids are, as a rule, strong poisons, but many of them are used in small doses as medicine.

Many qualitative group reactions of precipitation and colour reactions have been worked out for detecting alkaloids. For instance, many alkaloids are precipitated by phosphomolybdic acid, tannin, picric acid.

One of the structurally simplest alkaloids, *coniine* I, is α-propylpiperidine. Like all other alkaloids, coniine, which has the asymmetric carbon atom C-2, exists naturally in an optically active form. It is a liquid (b.p. 166°C) and a strong base which, with acids, forms salts. Coniine is very poisonous, and it paralyzes respiratory organs.


I


II

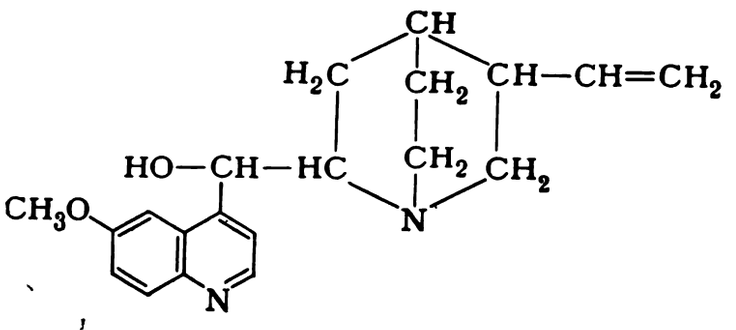

III

The alkaloid called *anabasine* II is also a pyridine derivative. This alkaloid was first separated by A. P. Orekhov (1928) from the plant called *anabasis aphylla*, which grows in Central Asia. At present, anabasine is obtained industrially in large amounts and is used as an insecticide.

Nicotine III is an anabasine isomer. It is the main alkaloid of tobacco, where it exists as salts of citric and malic acids. The levo-

rotatory antipode of nicotine, which is several times more poisonous than dextrorotatory nicotine, is found naturally. This is an interesting example of how the three-dimensional structure of organic substances affects their physiological properties. Nicotine (liquid, b.p. 246°C) extracted from tobacco is used as an insecticide. It is very poisonous for man as well, the mortal dose being about 40 mg.

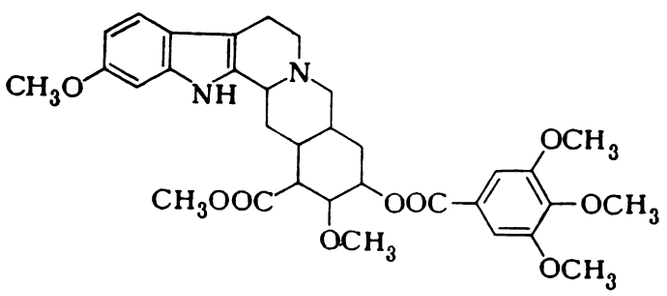
Quinine IV, an alkaloid of cinchona bark, is a derivative of quinoline:



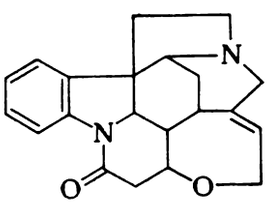
IV

Quinine became famous as a medicinal against malaria. Synthetic drugs, such as *acrichin*, are also used now against this disease.

Structurally, the foregoing examples are among the simplest alkaloids. The structural formulas of alkaloids can be very complicated, as is evident from that of *reserpine*, which is an alkaloid derived from the plant called *Rauwolfia serpentina*. Reserpine (separated in 1952) was the first preparation used to lower the blood pressure of patients with hypertension. It is also employed for treating mental disorders. *Strychnine* has a complex structure, which was elucidated by chemical methods in 1946 and confirmed by X-ray analysis in 1950. In 1954, the American scientist Woodward completely synthesized strychnine (30 stages). The formulas of reserpine and strychnine are given below merely to illustrate the complexity of the structure of these alkaloids, and not to remember them:



Reserpine



Strychnine

More than 1000 alkaloids are known. New alkaloids are being extracted from plants, and their structure is being ascertained, even now. Nevertheless, there is still no common opinion on the function of alkaloids in plants.

PART V

SPECIAL CHAPTERS ON ORGANIC CHEMISTRY

Chapter 22

ELEMENTS OF BIO-ORGANIC CHEMISTRY

At the beginning of the nineteenth century, chemistry was divided into inorganic and organic chemistry, the latter being a science of substances of plant and animal origin. Although much importance was later attached to the investigation of *synthetic* substances, i.e., substances which are not found naturally, organic chemists continued to investigate natural substances. As science developed, scientists solved problems of greater difficulty. In the nineteenth and the beginning of the twentieth centuries, the *chemical structure of substances* of plant and animal origin were studied at first, investigations were made of simple substances, and then of more complex ones. *Chemical processes* in living organisms were also studied on a growing scale. New sciences, i.e. *biochemistry* and recently *bio-organic chemistry*, originated at the point where chemistry and biology meet. It is difficult to make a clear distinction between the two given sciences, but it can be maintained that, in the main, biochemistry is a field of *biological science* in which chemical methods are used for studying phenomena in living organisms. Bio-organic chemistry deals with the chemical principles of vital processes. In this field, the most complex organic substances are encountered, and the most sophisticated methods of investigation are used.

22.1. Proteins. Amino Acid Composition. It has already been mentioned in the exposition of amino acids that high-molecular-weight compounds made out of amino-acid residues are called *proteins*. Proteins perform vital functions in all living organisms, whether of plant or animal origin. In the nineteenth century, F. Engels gave his well-known definition that life is a mode of existence of protein bodies. Although science has made great headway in the cognition of the essence of life, this definition has lost none of its importance today. Indeed, proteins are found wherever life exists.

The appearance and the physical state of proteins can be just as diverse as their functions in the organism. Egg albumin, muscles, the parts of the skeleton and of the joints, the skin, hair, horns and hoofs are different types of proteins. Proteins, including *hemoglobin*,

which transports oxygen, are found in a dissolved state in blood. Milk contains the protein called *casein* and a large amount of other proteins. Enzymes, which are very numerous and act as catalysts of metabolism in living organisms, are all proteins.

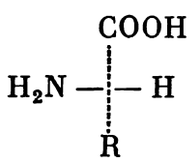
In plants, proteins do not perform "structural", as it were, functions. The polysaccharide called cellulose forms the core of the plant cell; nevertheless, proteins perform vital functions in plants, and they are concentrated mainly in seeds.

Notwithstanding the external dissimilarity, different proteins possess some common properties. For instance, solutions of all proteins are of a colloidal nature. The physico-chemical properties of proteins change (this process is known as *denaturation*) when temperature rises or when ultraviolet radiation, acids, alkalies and other reagents act on them. In this case, they lose their biological activity. Denaturation is now associated with changes in the conformation of protein molecules.

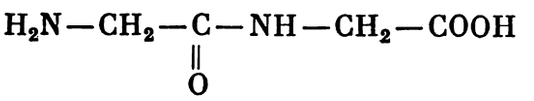
Proteins are precipitated by phosphotungstic, phosphomolybdic, picric, trichloroacetic, salicylic and other acids, and also by salts of many heavy metals. Proteins give many colour reactions as well. For example, specific colours originate when they react with alkaline solutions of copper salts (biuret reaction).

Twenty α-amino acids, which are given in Table 22.1, are the main constituent of proteins.

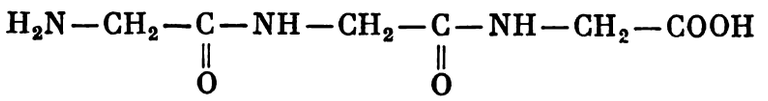
All protein amino acids except the simplest one, i.e., α-aminoacetic acid, have an asymmetric carbon atom in the molecule. Amino acids are present in an optically active form in proteins, and, by their configuration, they all relate to the L series, i.e., their three-dimensional structure is expressed by the following projection formula:



22.2. Protein Structure. Amino-acid molecules are linked in proteins according to the amide type. In this case, the bond is known as a *peptide* bond while compounds of the amide type, which are formed by several molecules of amino acids, are called *peptides*:

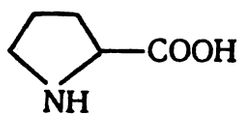
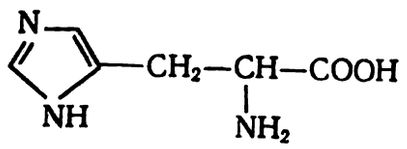
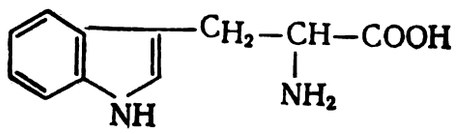
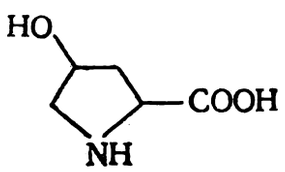


Dipeptide (Glycylglycine)

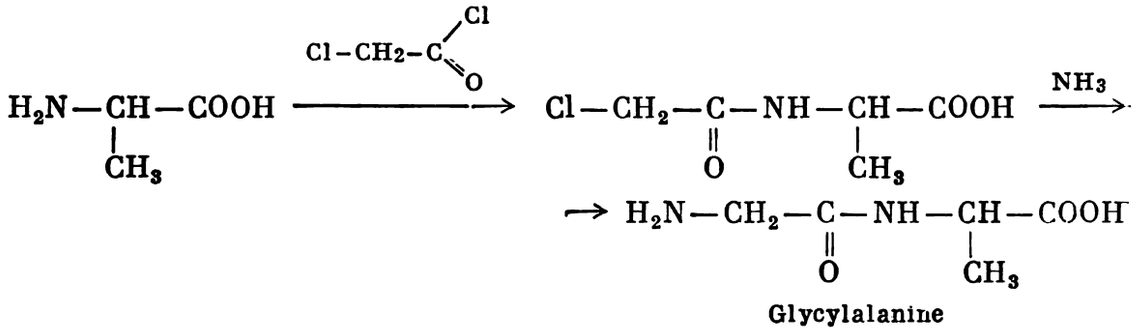


Tripeptide (Glycylglycylglycine)

TABLE 22.1. **Amino Acids in Proteins**

Formula	Name	Nominal notation
Monoaminomonocarboxylic acids	*Aliphatic*	
$H_2N—CH_2—COOH$	Glycine (glycocoll)	Gly
$CH_3—CH(NH_2)—COOH$	Alanine	Ala
$(CH_3)_2CH—CH(NH_2)—COOH$	Valine	Val
$(CH_3)_2CH—CH_2—CH(NH_2)—COOH$	Leucine	Leu
$C_2H_5—CH(CH_3)—CH(NH_2)—COOH$	Isoleucine	Ileu
	Aromatic	
$C_6H_5—CH_2—CH(NH_2)—COOH$	Phenylalanine	Phe
	Heterocyclic	
	Proline	Pro
	Histidine	His
	Tryptophan	Try
Monoaminodicarboxylic acids		
$HOOC—CH_2—CH(NH_2)—COOH$	Aspartic acid	Asp
$HOOC—CH_2—CH_2—CH(NH_2)—COOH$	Glutamic acid	Glu
Diaminomonocarboxylic acids		
$H_2N—(CH_2)_4—CH(NH_2)—COOH$	Lysine	Lys
$HN=C(NH_2)—NH—(CH_2)_3—CH(NH_2)—COOH$	Arginine	Arg
Hydroxyamino acids		
p-$HO—C_6H_4—CH_2—CH(NH_2)—COOH$	Tyrosine	Tyr
	Hydroxyproline	Hyp
$HO—CH_2—CH(NH_2)—COOH$	Serine	Ser
$CH_3—CH(OH)—CH(NH_2)—COOH$	Threonine	Thr
Mercaptoamino acids		
$CH_3S—CH_2—CH_2—CH(NH_2)—COOH$	Methionine	Met
$HS—CH_2—CH(NH_2)—COOH$	Cysteine	Cys
$S—CH_2—CH(NH_2)—COOH$ $\vert$ $S—CH_2—CH(NH_2)—COOH$	Cystine	Cys-Cys (Cy—S—S—Cy)

In the foregoing examples, the composition of peptides includes residues of the same amino acids (the simplest one of them, glycine); peptides of greater complexity contain residues of different amino acids. Peptides can be synthesized, for instance, by acylating amino acids by means of chlorides of halogenated acids and the subsequent action of ammonia:



Glycylalanine

By consistently using such reactions, E. Fischer obtained, in his classical investigations, peptides which had up to 18 amino-acid residues.

Since then, many other ways of synthesizing peptides have been worked out. What all these syntheses have in common is that the interacting groups, i.e., carboxylic and amino groups, are converted into an active state in one way or another (in Fischer's synthesis, this is attained by conversion into an acid chloride), while the remaining functional groups are "protected", i.e., they are converted temporarily into inactive derivatives whenever this is necessary. An active functional group is obtained again by "removing protection", and it can be used for further building up the peptide chain.

The molecular mass of proteins ranges from several thousands to several millions, i.e., the number of amino-acid residues in the protein macromolecule ranges from several tens to hundreds of thousands. For example, the natural polypeptide called oxytocin, a hormone which is excreted by the posterior lobe of the pituitary gland, consists of nine amino acids, and its molecular mass is 1007; the molecular mass of the adrenocorticotropic hormone (23 amino acids) is 3200, that of the enzyme ribonuclease (124 amino acids) is 15,000, and that of hemoglobin (blood protein) is 68,000, while that of viruses proteins can be as much as 50 millions. Even these variations create great diversity in proteins. But a far more important cause of the diversity of proteins in comparison with, say, polysaccharides is that the protein macromolecule can have about 20 *different amino acids*, while ordinary polysaccharides (cellulose, starch) are made out of *one monosaccharide*: glucose.

The diversity of proteins can be seen by counting the number of different decapeptides (i.e., polypeptides having ten amino-acid residues) that can be built from 20 known protein amino acids. The

figure obtained is the number of arrangements of 20 elements in a group of ten elements. The calculation made by the formula

$$A_m^n = m\,(m-1)\,(m-2)\,\ldots\,[m-(n-1)]$$

($m = 20$; $n = 10$) gives a value of the order of 600 billions. But this calculation is for a rather simple polypeptide which has a molecular mass of the order of 1500-2000.

Scientists are now trying to elucidate the *chemical structure of specific proteins*, and are synthesizing them. For instance, two protein hormones, *oxytocin* and *vasopressin*, were synthesized as early as the 1950's. They are comparatively simple polypeptides, i.e., each of them has nine amino-acid residues.

Scientists have ascertained the structure of the protein hormone called *insulin*, which controls glucose metabolism in the organism, and the structure of *ribonuclease*, an enzyme which catalyzes the hydrolytic cleavage of ribonucleic acids (see Sec. 22.4) into simple nucleotide residues. A report on the synthesis of this enzyme appeared in 1969.

The achievements which have now been made in deciphering the protein structure are not confined to the foregoing examples. An investigation is being made especially of proteins which act as catalysts of chemical processes in living organisms, i.e., *enzymes* and *hormones*. A comparison of the results has shown that the carrier of biological activity is, in some cases, not the entire protein molecule, but a definite part of it. For instance, the plant enzyme called papain, which is composed of 180 amino-acid residues, can be "shorn" to two-thirds of its polypeptide chain without noticeably affecting its biological activity. Such facts give us a better understanding of the nature of the catalytic action of enzymes and a good reason to believe that it is possible to create synthetic enzymes which will make it easier to obtain many organic substances that are necessary for Man. Another important fact is that researchers, after learning how to synthesize proteins, can, besides reproducing natural products, synthesize substances which are *similar* to natural ones, but which differ from them in a certain way. When there is a series of such analogues, an eye can be kept on the changes in their physiological activity, depending on the changes in their chemical structure, and this is important both theoretically and practically.

A study of the structure of proteins, which perform important physiological functions, has, in some cases, revealed the primary chemical cause of some diseases. For instance, in sickle-cell anemia, a serious hereditary illness, the hemoglobin is anomalous: *only one* amino acid is replaced by another in the complex chain of this blood protein. Several such "molecular diseases" (a term proposed by the famous American scientist Pauling) are known today.

Such observations still cannot be used in practice today, but they are obviously of great importance to biology as well as medicine.

The *simple proteins* are substances which give only amino acids in hydrolysis. In biochemistry, they are subdivided into many groups (e.g., albumins, globulins, protamins, glutelins) in conformity with their properties and biological functions.

The *conjugated proteins*, or complex proteins, are compounds of proteins with a nonprotein part called a prosthetic group. There are the following groups of conjugated proteins, depending on the nature of the nonprotein part:

1. *Phosphoproteins* contain phosphorus. The most important representative of this group is *casein* from milk.
2. *Lipoproteins* are compounds of proteins with derivatives of fatty acids, i.e., phosphatides, sphingomyelins, and polyene pigments of the carotene type. Proteins of this type include, for instance, *visual purple.*
3. *Glycoproteins* and *mucoproteins* are compounds of proteins with carbohydrates; the conjugated proteins of this type include *serum albumins*, *serum globulins* and *hyaluronic acid* of the glassy liquid of the eye.
4. *Chromoproteins* are complex proteins which have complexly bonded metal. Proteins of such a type are *hemoglobin*, which contains iron and is the respiratory pigment of mammalian blood, and *hemocyanins*, which contain complexly bonded copper and are the respiratory pigments of the blood of mollusks, snails, crabs, etc.
5. *Nucleoproteins* are compounds of proteins with nucleic acids. A separate section on them has been written, because they are very important.

The amino-acid composition and the sequence of the amino-acid bond in the molecule of a protein determine its *primary structure.* For example, the primary structure of oxytocin, a protein hormone,

$$\begin{array}{cc} NH_2 & NH_2 \\ | & | \end{array}$$

is expressed by the following scheme (the abbreviations Glu and Asp stand for glutamine and asparagine, i.e., amides of the respective amino acids):

$$\begin{array}{cccccccccccc} & & & & NH_2 & NH_2 & & & & & & \\ & & & & | & | & & & & & & \\ Cys & - & Tyr & - & Ileu & - & Glu & - & Asp & - & Cys & - & Pro & - & Leu & - & Gly & - & NH_2 \\ | & & & & & & & & & & | & & & & & & & & \\ S & - & - & - & - & - & - & - & - & - & S & & & & & & & & \end{array}$$

The properties of proteins in their native state are determined not only by the primary structure; the three-dimensional structure of the protein molecule is also of great importance. The polypeptide chain can have different conformations, e.g., it can exist in the form

of an α-helix (Fig. 22.1). The conformational varieties of the polypeptide chain determine the *secondary structure* of a protein.

A chain which has a definite conformation (a definite secondary structure) can fold or twist further with the formation of a *tertiary*

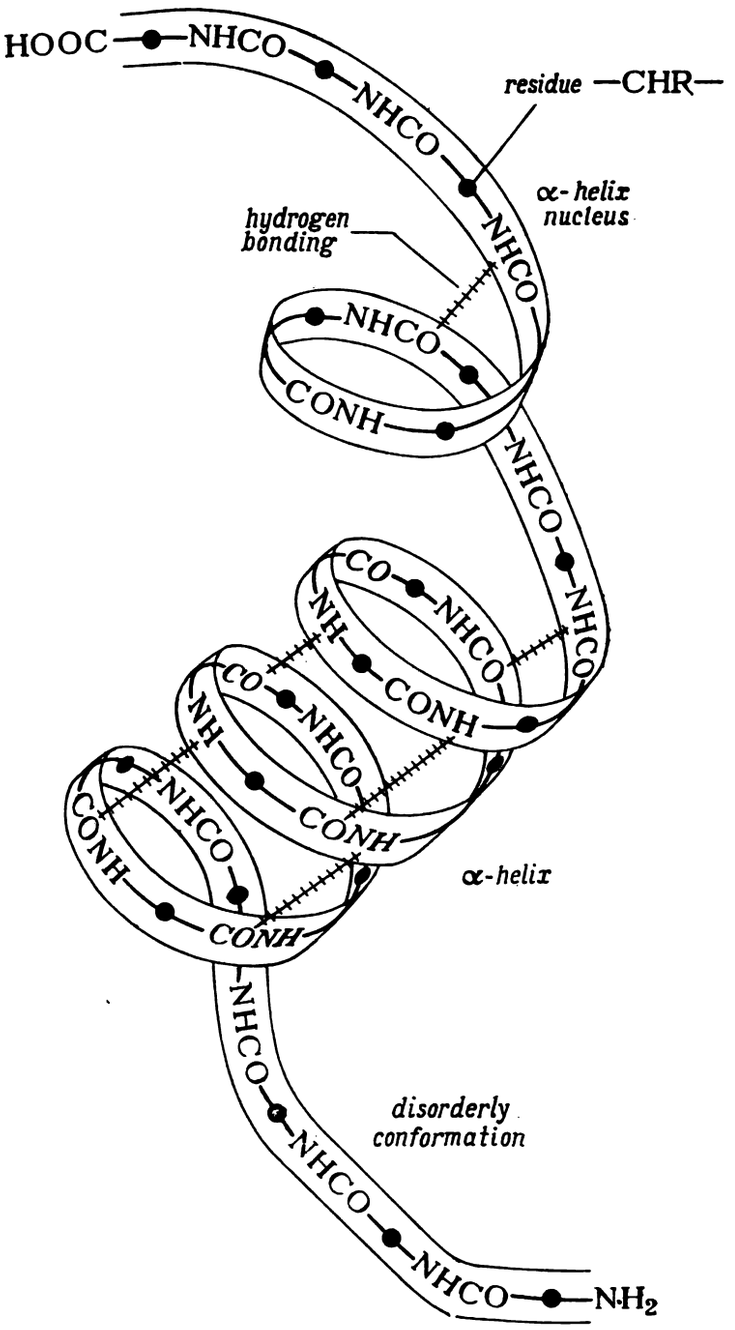
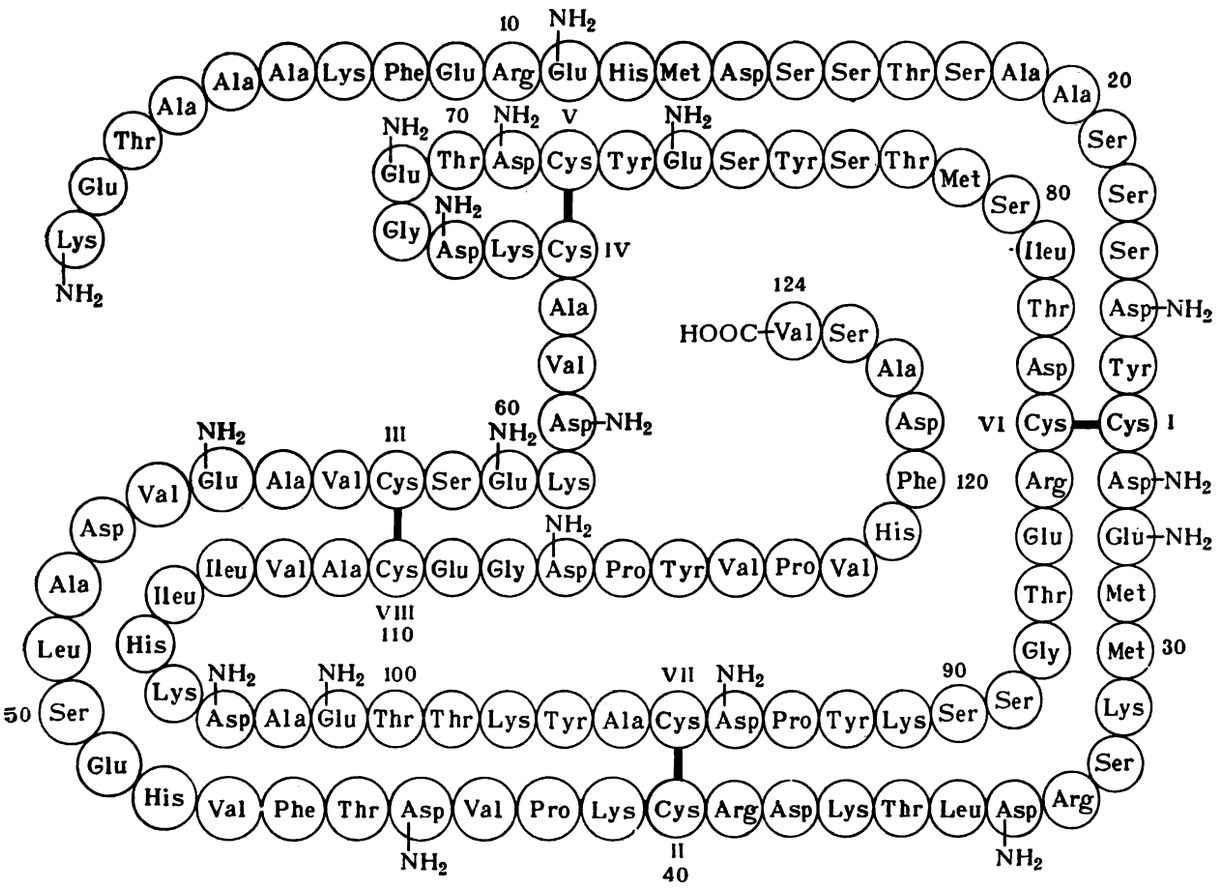
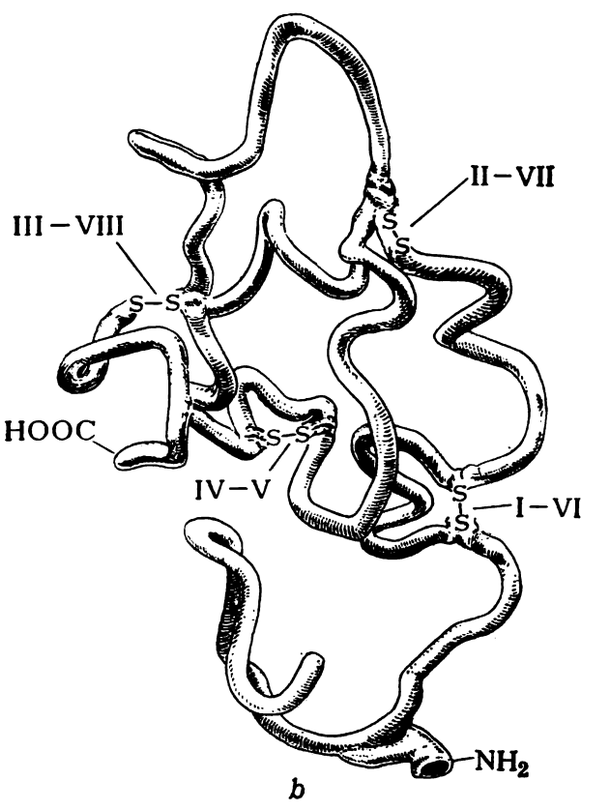


Fig. 22.1. Protein α-helix

structure. For example, Fig. 22.2 shows the tertiary structure of an enzyme ribonuciease, which is a polypeptide made out of 124 amino-acid residues.


10 NH2
Ala Ala Lys Phe Glu Arg Glu His Met Asp Ser Ser Thr Ser Ala Ala 20
Ala Thr Glu Lys NH2
Ser Ser Asp NH2 Tyr
70 NH2 V NH2
Glu Thr Asp Cys Tyr Glu Ser Tyr Ser Thr Met Ser 80
NH2
Gly Asp Lys Cys IV
Ileu Thr Asp Cys Cys I
124
HOOC Val Ser Ala Asp Phe 120
Val Asp Asp NH2
60
Ala Val Asp NH2
III NH2
NH2 Glu Ala Val Cys Ser Glu Lys
Arg Glu Thr Gly
Asp Glu NH2 Met Met 30
His
NH2
Ileu Val Ala Cys Glu Gly Asp Pro Tyr Val Pro Val
VIII
110
Ileu
His
Leu
Lys
NH2 NH2 100 VII NH2 90
Asp Ala Glu Thr Thr Lys Tyr Ala Cys Asp Pro Tyr Lys Ser Ser
Lys
50 Ser
Glu
Ser
His Val Phe Thr Asp Val Pro Lys Cys Arg Asp Lys Thr Leu Asp Arg
NH2
II
40
NH2

a



b

Fig. 22.2. Amino acid sequence (*a*) and the tertiary structure (*b*) of ribonuclease.
Roman numerals stand for the residues of cysteine between which the S-S bond is formed

Proteins lose their "natural" properties under the action of heat and chemical reagents even if there are no chemical changes in this case. Such a process, known as *denaturation*, is connected with changes in the tertiary and secondary structures.

22.3. Use of Proteins as Food and in Industry. Plants are capable of synthesizing amino acids and proteins by using inorganic compounds as the nitrogen source. But animals must get proteins from food in order to exist normally. In digestion, proteins are split into low-molecular peptides or amino acids, which are absorbed by the intestine and then carried by the blood flow. They are building blocks from which the organism creates proteins of its own body. Thus, proteins in food can be replaced by amino acids quite well. The organism can produce some amino acids which are indispensable for life from other nitrogen-containing compounds which enter into it together with food. But the organism is incapable of synthesizing other amino acids, and they must be introduced in prepared form together with protein food. Such amino acids are called *essential*. They include *lysine*, *tryptophan*, *phenylalanine*, *valine*, *methionine*, *threonine*, *leucine*, *isoleucine*, *histidine*, and *arginine* (see Table 22.1).

Protein food should not only satisfy the general requirement for amino acids as the main "building blocks" of the organism, but also contain the required quantities of essential amino acids. The organism cannot function normally when there is a shortage of essential amino acids.

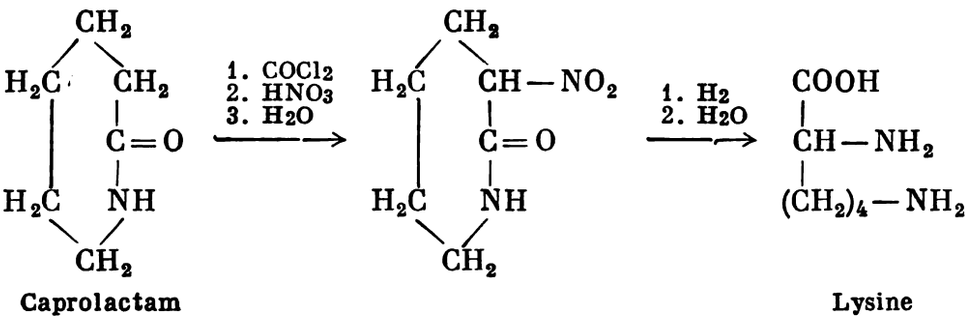
For example, *zein*, which is a maize protein, does not contain lysine and has almost no tryptophan. Experiments on animals receiving only this protein with food showed that they lost weight even if much food were given. When food does not contain tryptophan, an eye disease called cataract develops.

Man satisfies his requirement for proteins by eating vegetables, meat and fruits. But agriculture is hardly an ideal source of food, because it depends on natural conditions and requires large areas of land and much human labour. Therefore, scientists have long been considering the *synthesis of food products*, especially proteins, which are the most valuable part of food.

The microbiological synthesis of proteins from petroleum hydrocarbons is now most promising. In the late 1950's, microorganisms which can feed on paraffin hydrocarbons were discovered. Thus, 0.7 ton of rich proteins is obtained from one ton of hydrocarbons. The mass formed contains also vitamins of the B group.

The method of obtaining protein-vitamin concentrates from petroleum has been mastered industrially in the Soviet Union. The raw materials used are heavy petroleum fractions with additives of ordinary potassium, nitric and phosphoric fertilizers, and also trace elements. Microorganisms process this mixture into a protein mass, which is used in livestock breeding.

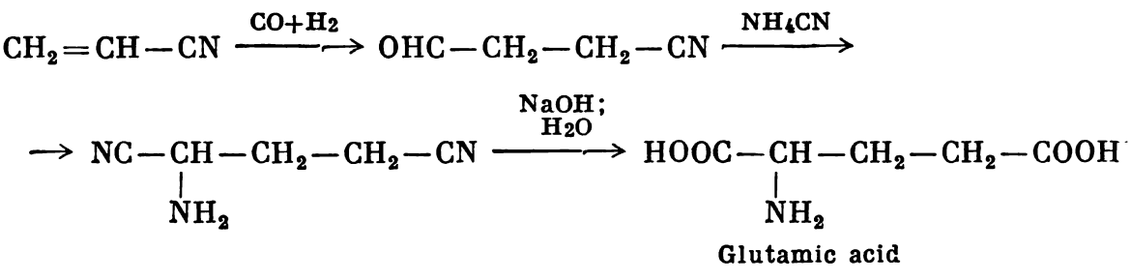
Amino acids in the "shortest supply" are now added to the food of farm animals in order to increase their food value. For this purpose, lysine, glutamic acid and methionine are being produced industrially on a large scale. To synthesize lysine, use is made of caprolactam, which is raw material also for producing capron. A nitro group is introduced into it (the process occurs in several stages), and then it is reduced with a simultaneous break in the lactam cycle:



Caprolactam Lysine

A shortage of lysine in food causes anemia, headache and high irritability. Synthetic lysine is put into children's food to increase their appetite, and it is used for treating serious poisonings. In livestock breeding, it is added to fodder.

Glutamic acid is produced industrially on the basis of acrylonitrile. Synthesis occurs according to the following scheme:



Glutamic acid

Glutamic acid is added to tinned food and food concentrates in order to improve their taste.

Other components of food can be obtained synthetically, too. Both components of fats, i.e., glycerol and fatty acids, are already being produced industrially from petroleum. There are no fundamental difficulties also in obtaining fats from these components.

Vitamins, an indispensable component of rich food, are now being synthesized on an industrial scale.

The prospects of synthesizing food carbohydrates are not clear in the least, because a definite stereoisomer, glucose, must be obtained,

and this is difficult. But glucose is now being obtained from raw material other than food, i.e., from wood, by hydrolysis.

All the components which must be contained in rich food are now known. Mixtures prepared from them have been used experimentally to feed animals, which live indefinitely on such a diet. Such mixtures have been tried out also in people's long nourishment.

Academician A. N. Nesmeyanov, who initiated the elaboration of the synthetic food problem in the Soviet Union, said that it is like "planting a tree whose top goes high into the future, while its roots are in the soil of the present and await the greatest care".

Proteins are important not only as food, but also as industrial material. The tanning industry is the largest industry which processes protein raw material. Silk and wool are also proteins. The protein called casein, which is separated from milk, is used for making glue. Plastic obtained from casein (Galalith) was formerly of great importance, and attempts were made to obtain even artificial fibre from casein. Proteins include *gelatin*, which is used for producing cinematographic materials.

22.4. Structure and Properties of Nucleic Acids. It had been ascertained as early as the nineteenth century that cell nuclei have high-molecular-weight substances whose composition includes nitrogen-containing heterocyclic bases, carbohydrates and phosphoric acid. These substances had been termed *nucleic acids*. A few decades ago, the biological importance of nucleic acids had not been clear at all, but now their cardinal importance in nature has been ascertained.

Nucleic acids are high-molecular-weight compounds (their molecular mass ranges from 200,000 to several millions). Complete acid hydrolysis of a nucleic acid yields a mixture of phosphoric acid, a sugar component, usually ribose and deoxyribose, and heterocyclic base components, purine and pyrimidine bases.

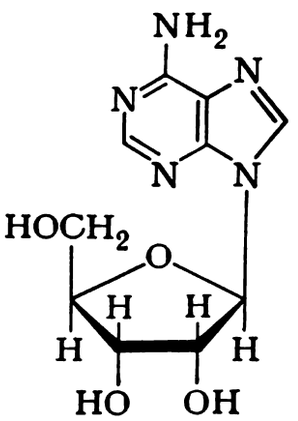
A mixture of substances called nucleotides is formed when nucleic acids undergo milder hydrolysis. The *nucleotide* composition includes residues of the pyrimidine or purine base, a pentose and phosphoric acid. Phosphoric acid can be eliminated from nucleotide; this produces *nucleoside*, which consists of the purine (or pyrimidine) base and a pentose.

It follows that *nucleotides* are the monomer unit of nucleic acids. These substances are divided into deoxyribonucleotides and ribonucleotides in conformity with the nature of a pentose which is in the nucleotide composition.

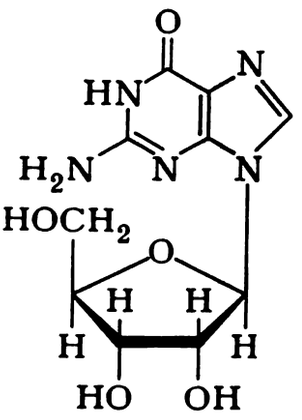
Deoxyribonucleotides have *deoxyribose* in their composition. Polymers of deoxyribonucleotides are known as *deoxyribonucleic acids* (DNA).

Ribonucleotides have *ribose* in their composition. Polymeric ribonucleotides are *ribonucleic acids* (RNA).

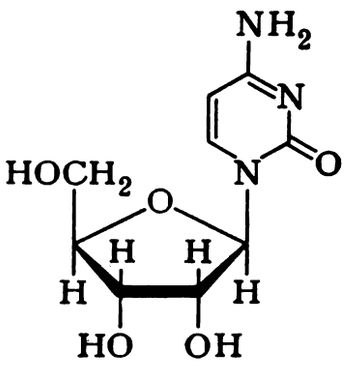
Nucleosides in RNA are given below:



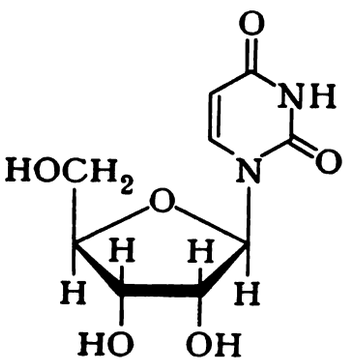
Adenosine



Guanosine



Cytidine



Uridine

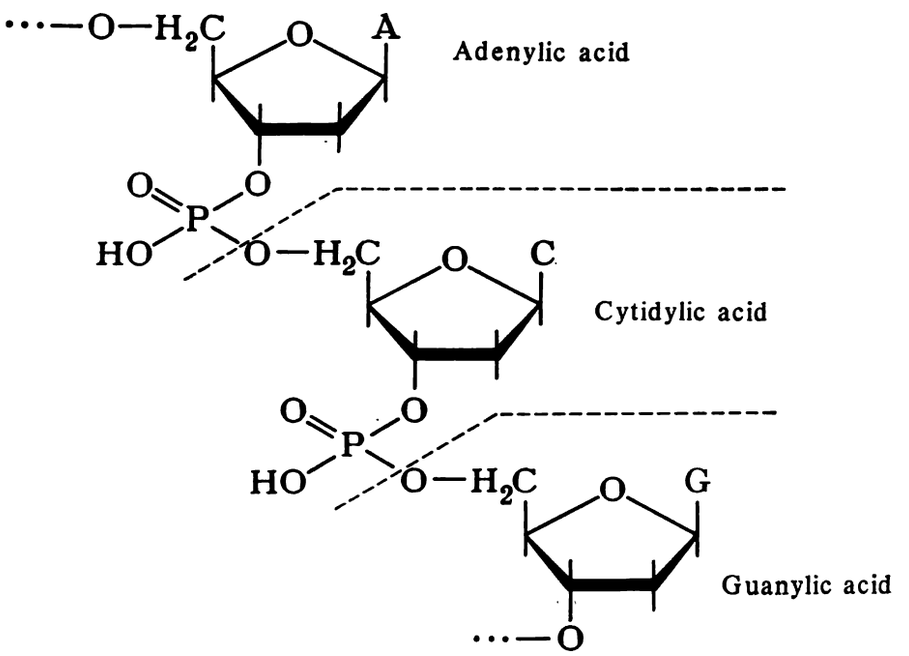
These nucleosides are structurally N-β-glycosides of D-ribose. They include two purine bases (*adenine* and *guanine*) and two pyrimidine bases (*cytosine* and *uracil*).

The composition of deoxyribonucleic acids (DNA) includes nucleosides, which are built like the foregoing ones, but which contain 2-deoxyribose* instead of ribose. Moreover, the fourth nitrous base of DNA is *thymine* instead of uracil, which is present in RNA.

Macromolecules of DNA and RNA themselves are high polymers in which nucleosides are linked, from the C-3 to C-5 position, by

* The prefix "2-deoxy" indicates the absence of a hydroxyl group at C-2.

phosphate ester linkages. A fragment of a DNA molecule with residues of adenine (A), cytosine (C) and guanine (G) is given below as an example:



22.5. Biological Importance of Nucleic Acids. Their biological importance began to be clarified in the 1940's, when it was first ascertained that DNA taken from one variety of bacteria and introduced into another forces the latter to produce progeny with signs of the first variety. It followed that "hereditary information" was conveyed with DNA, i.e., there was an order, coded in some way, to build protein molecules of a definite type.

These investigations became the starting point of rapid progress in "molecular genetics", which give us an insight into protein synthesis in cells, the reproduction of cells by division, and ultimately the reproduction of the entire complex animal or plant organism in a form which is characteristic of its parents. A detailed discussion of these problems would take us far into the biochemical field; generally, the role of DNA and RNA is as follows.

DNA molecules are in cell nuclei. They contain genetic information, which is coded as a different sequence of nucleotides. DNA acts as a template from which copies of RNA molecules, which participate in protein synthesis, are replicated. Thus, RNA molecules act as messengers of information from DNA to cell sites where protein synthesis is being effected.

The importance of RNA in protein synthesis was confirmed by

experiments carried out in the early 1960's. A liquid without cells was obtained from the cells of the bacterium *Echerichia coli* after it was completely destroyed; the liquid contained all the enzymes which were needed for protein synthesis and were formely in the cell. This system is capable of effecting protein synthesis for some time, and then this synthesis becomes retarded. Protein synthesis begins again if RNA is added at this moment. It follows that RNA participates in protein synthesis.

When this was ascertained, *synthetic* RNA instead of natural RNA began to be added. Protein synthesis continued in this case as well. When synthetic RNA containing only nucleotide, i.e., uracil, was added, a peptide consisting almost entirely of a single amino acid, phenylalanine, was formed.

Further experiments in this field made it possible to decipher the "genetic code", i.e., they made it possible to determine how the "order" to incorporate definite amino acids into a protein molecule is coded in the RNA molecule. Every amino acid has its own "code" which is registered in the form of a sequence of three out of four nucleotides which are found in RNA molecules: adenosine (A), guanosine (G), cytidine (C) and uridine (U). For instance, the incorporation of alanine is set by one of the three codes CCG, UCG and ACG, the incorporation of tryptophan, by the code GGU etc.

In the last decades, extraordinary scientific achievements have been made in the study of the structure of protein and the ways of synthesizing it in living organisms. A few decades ago, disputes were still held on the general principles of protein structure, while now the chemical structure of *specific proteins* is being elucidated and amino acids combinations of ever greater complexity are being synthesized. Recently, nothing had been known about the biochemical importance of nucleic acids, while now human knowledge has fathomed deeply into the mechanism of protein biosynthesis, although many problems have to be solved yet. Thus, science is rapidly gaining an insight into the chemical nature of the most secret vital processes. This holds out great prospects for medicine, especially in fighting malignant tumours.

22.6. Enzymes. Enzymes act as catalysts of chemical transformations in animal and plant organisms. The catalytic action of enzymes is characterized by high effectiveness and strict direction. These properties enable them to rapidly effect complicated transformations of organic substances under mild conditions as well, i.e., at low temperature and standard pressure, in dilute solutions, and when the reaction of a medium is close to a neutral one. Therefore, the study of enzymes, besides being important biochemically, can show the ways of producing highly effective catalysts for industry.

More than a thousand enzymes are now known, and each of them is a catalyst of a definite reaction.

Enzymes are related chemically to proteins. In their molecules, the protein part is connected with the nonprotein component, which is known as a *coenzyme*.

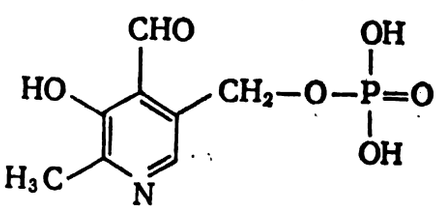
The chemical structure of many coenzymes is known. The mechanisms of their transformations in the realization of catalytic functions have also been studied. But this does not mean that the catalytic role of the enzyme has been completely ascertained. The fact is that the coenzyme usually either does not have catalytic properties at all or exhibits them only slightly. The coenzyme becomes active only in combination with the corresponding protein. It is still not quite clear how this occurs. In general, the mechanism of the catalytic action of an enzyme is believed to be the following.

The coenzyme, together with definite parts of a protein molecule, forms an active centre. All the components of this centre are at strictly definite distances away from one another and occupy a definite place in space. The formation of the active centre is in conformity with the structure of the molecule (substrate) whose transformation catalyzes the given enzyme. This creates favourable conditions for the formation of an enzyme-substrate complex, and then bonds are broken and new ones are simultaneously formed.

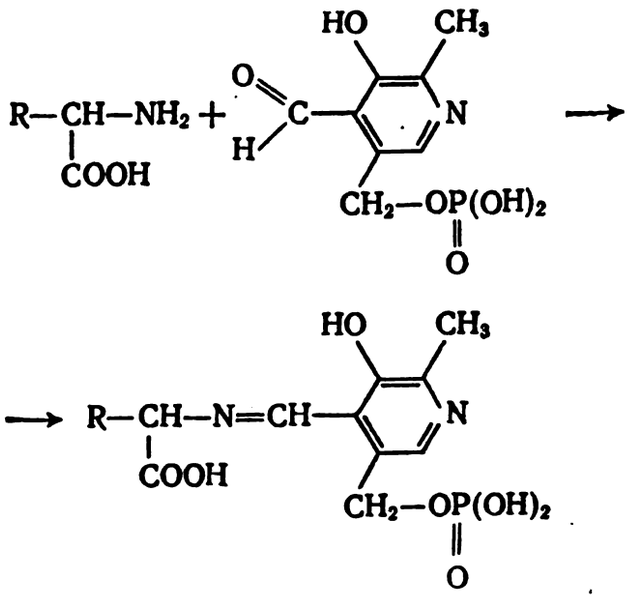
Enzymes in living organisms are partially in a dissolved state, but, in many cases, they form strictly organized systems, or conveyer belts, as it were, on which chain chemical transformations occur; these transformations ensure, for example, respiratory processes, digestion, and the construction of proteins and other substances that are indispensable for the organism.

The number of the coenzymes known is far less than that of the enzymes known: the same coenzyme in combination with diverse proteins can form different enzymes. Many coenzymes are related chemically to the *nucleotide* class, while others contain the *porphyrin* cyclic system, i.e., a heterocyclic arrangement of four pyrrole nuclei, which are found, for instance, in chlorophyll and hemoglobin (p. 429), many important enzymes relate to phosphorus-containing compounds.

Several enzymes, which catalyze various conversions of amino acids, such as their synthesis, transamination and decarboxylation, contain the coenzyme called *pyridoxal-5-phosphate*:

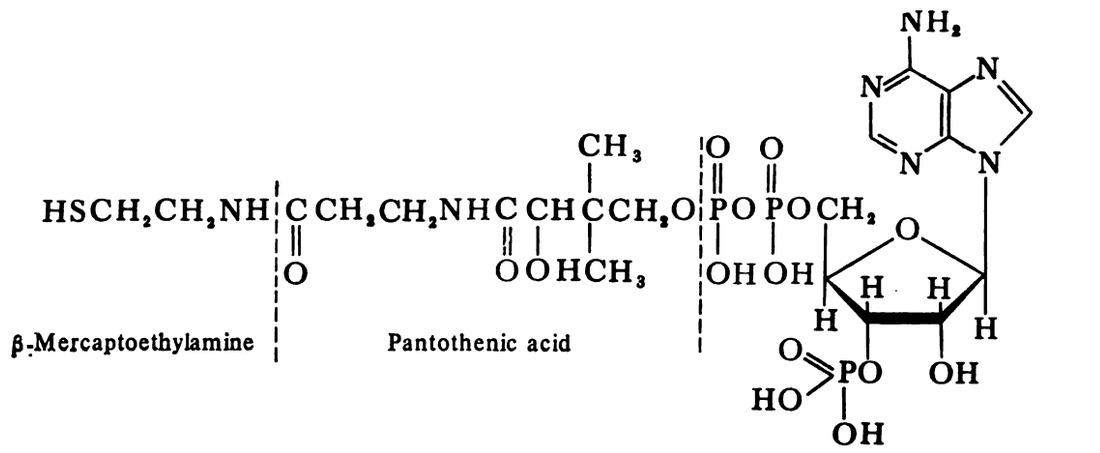


In all these conversions, the aldehyde group of the coenzyme reacts first of all with the amino group of amino acid:



The nature of further conversions depends on the specific nature of an enzyme, i.e., on the structure of its protein part.

Let us consider the *coenzyme* A as an example of greater complexity. It is a white amorphous substance which dissolves well in water and has the composition of $C_{21}H_{36}O_{16}N_7P_3S$. Its chemical structure is expressed by the formula:



β-Mercaptoethylamine | Pantothenic acid | Adenosine phosphate residue

The coenzyme A participates in more than 60 reactions, which include the synthesis of fatty acids and their oxidation, the synthesis of acetylcholine and citric acid, and the cleavage of pyroracemic acid.

Enzymic preparations are very important industrially as well. The preparation of cheese, tea and tobacco, leather dressing, and wine-making are enzymic processes.

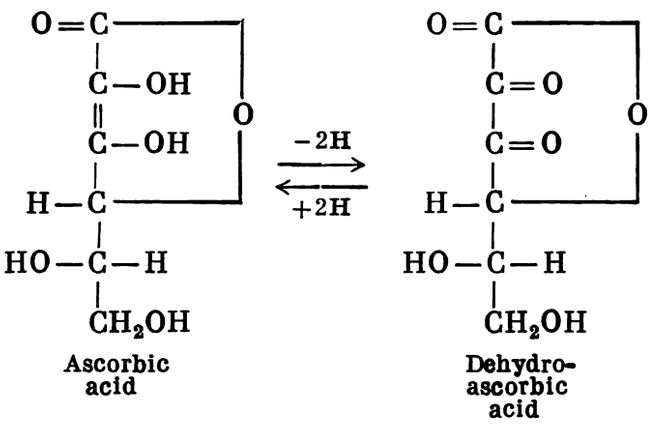
Enzymatic transformations occur at room temperature, and they do not require high pressure and active reagents; this is true, for instance, of the fixation of atmospheric nitrogen by tuber bacteria. Many technological problems could be solved if the mechanism of enzymic action were discovered and reproduced under industrial conditions. One way of doing this is by using *immobilized enzymes*, i.e., enzymes which are fixed on polymeric carriers. In this case, enzymes become more stable.

22.7. Vitamins. The term "vitamins" (from the Latin word "vita", meaning "life") was applied to constituents of food which are negligible in it, but which are indispensable for the normal existence of animals and Man. When the chemical nature of vitamins was still unknown, they were denoted by letters of the Latin alphabet. Although the structure of vitamins has now been ascertained, they are still denoted by the usual letters instead of long chemical names.

More than 20 vitamins are now known, and their chemical structure and the role which they play in the organism have been ascertained. It turned out that many vitamins are used in enzymic synthesis.

Vitamins are divided into water-soluble (vitamin C, vitamins of the B group, vitamin PP, and some others) and fat-soluble (vitamins of the A, D and K groups) ones.

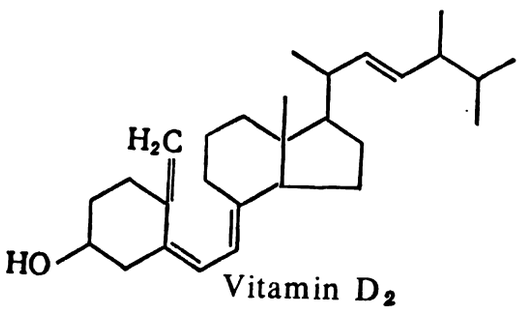
Vitamin C (*ascorbic acid*) is a substance related chemically to saccharides. It is contained in fresh fruits and vegetables, but is obtained also synthetically from the hexahydric alcohol called sorbitol, $CH_2OH—(CHOH)_4—CH_2OH$. A deficiency of this vitamin causes scurvy. The principal chemical property of ascorbic acid is the ability to be readily oxidized with the formation of dehydroascorbic acid, which can be readily reduced to ascorbic acid:



Ascorbic acid — Dehydroascorbic acid

The main function of ascorbic acid in the organism is participation in oxidation-reduction transformations accompanied by hydrogen transfer.

Vitamin D_2 (*calciferol*). A deficiency of this vitamin causes rickets. It is contained in fat products (animal and fish liver oil).

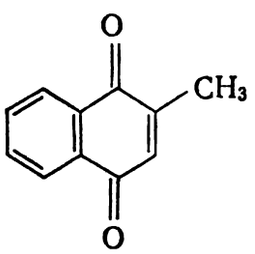


Vitamin D_2

The daily requirement for this vitamin is about 0.025 mg; the consumption of very large amounts of vitamin D_2 (like other fat-soluble vitamins) is detrimental to the organism.

Vitamin D_2 is not only extracted from natural products, but also obtained synthetically. The starting substance for its synthesis is *ergosterol*, i.e., a polycyclic compound which belongs to the steroid class (see Sec. 22.10). Ergosterol is transformed into vitamin D_2 under the action of ultraviolet light. Such a process apparently occurs also directly in the organism under the action of sunlight.

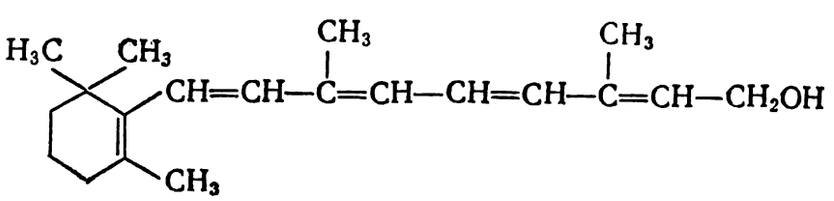
Vitamins K are a group of structurally and physiologically related compounds which are naphthoquinone derivatives. The simplest one is *vitamin* K_3, or 2-methyl-1,4-naphthoquinone I:



I

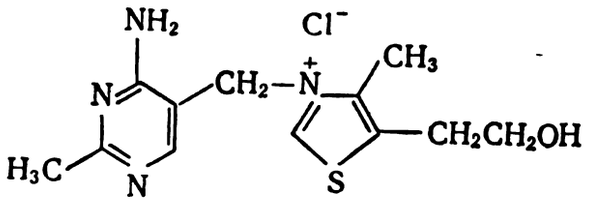
This vitamin is capable of coagulating blood.

Vitamin A (*retinol*) II protects against the eye disease called xerophthalmia and acts as a growth-stimulating vitamin. It is formed in the organism from a yellow dyeing substance called carotene (which is contained in carrots):



II

Vitamin B_1 (*thiamine*) III protects against the disease called beriberi. It is contained in rice husks, yeast, and wheat shoots.

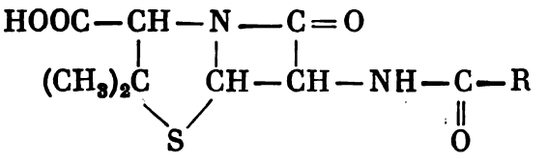


III

22.8. Antibiotics. Antibiotics, which are effective medicinals produced by microorganisms, were discovered at the end of the 1930's. About 500 antibiotics have now been separated. The structure of many of them has been ascertained, while the chemical nature of others is still being studied. Antibiotics are now the strongest medicinals against infectious diseases.

Antibiotics may differ in their chemical nature; they include compounds of the heterocyclic and aromatic series as well as substances of a polypeptide structure.

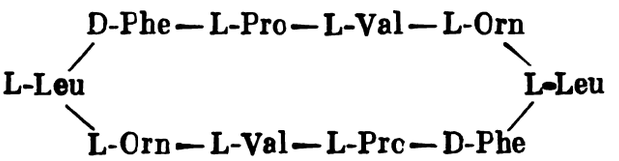
Penicillin is historically the first antibiotic; it was discovered in Britain in 1940. Its structure is based on a five-membered heterocycle called thiazolidine, which contains the nitrogen atom and the sulphur atom:



Penicillin

Several penicillins, which differ from one another by the nature of the radical R in the side chain, are now known. These antibiotics have a rather narrow range of action, i.e., they hinder the development of only definite microorganisms.

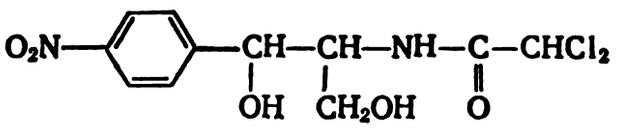
In 1942, the Soviet scientists Gause and Brazhnikova separated *Gramicidin* S (gramicidin Soviet) from soil microorganisms. This antibiotic also has a narrow range of action. Gramicidin has a polypeptide structure, i.e., it is built out of amino-acid residues which are linked by amide bonds:



Gramicidin S

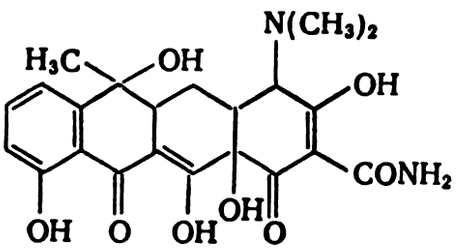
Chloromycetin has a very peculiar structure for a natural substance. It is a benzene derivative whose molecule includes a nitro group and

a dichloroacetic-acid residue:



This compound has two asymmetric carbon atoms and can exist as four stereoisomers. But only one isomer has antibiotic activity. This fact confirms that the physiological action of organic substances depends on their three-dimensional structure. Chloromycetin is now synthesized.

Tetracyclines constitute an important group of antibiotics. The name indicates their structure, i.e., the molecule has four condensed six-membered cycles:



Tetracycline

This group of antibiotics is characterized by a wide range of action. They are used against the most diverse microorganisms.

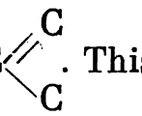
The treatment of various diseases has shown that microorganisms get *accustomed* to antibiotics: new races of microorganisms gradually appear, and a definite, usual antibiotic can no longer act on them. This can create difficulties in treatment, and the producers of new antibiotics and the microorganisms which are protecting themselves must continue to "compete" with one another.

22.9. Terpenes. Terpenes are substances of a hydrocarbon, alcohol or ketone nature that are in the essential oils of plants. Most terpenes are derivatives of alicyclic hydrocarbons, although some open-chain compounds also belong to terpenes.

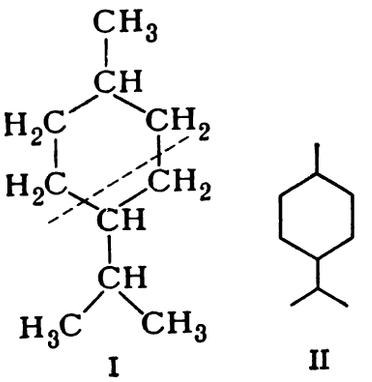
Terpenes are, as a rule, liquids with a pleasant odour, practically insoluble in water. Their ability to be distilled with water vapour is used to separate essential oils from plants.

Turpentine, a mixture of terpenes, is obtained by distilling conifer resin, or *oleoresin*. This resin is collected by making incisions on the trunks of fir, pine and cedar. Turpentine is used as raw material for obtaining individual terpene hydrocarbons, mainly *α-pinene*. In addition, turpentine is used as a solvent for lacquers, paints and

enamels, and as an agent for obtaining lubricants, flotation oils, pesticides, insecticides, and medicinals.

Terpene hydrocarbons relate to *isoprenoid compounds*, which are widely distributed in nature and whose structure is based on the isoprene unit  . This group of compounds includes natural rubber (Sec. 23.5).

Most terpenes are based on the cyclohexane hydrocarbon called *p-menthane* I, which is built, as it were, out of two isoprene radicals. The formula for menthane is often represented conventionally (formula II):



I

II

Terpenes which are directly based on the hydrocarbon menthane are called *monoterpenes*; they have ten carbon atoms in their composition. The carbon skeleton may be either acyclic or cyclic. The terpenes C_{15} are called *sesquiterpenes*, C_{20}, *diterpenes*, and C_{30}, *triterpenes*. All these compounds have a cyclic structure. Triterpenes have up to five condensed six-membered rings.

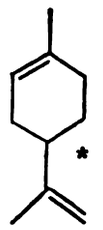
Terpenes are divided into *acyclic*, *monocyclic*, *bicyclic* and *polycyclic* ones depending on the nature of the carbon skeleton.

Besides the hydrocarbons proper, alcohols, ketones and acids, which belong to the terpene class, are found naturally. Only the simplest representatives of mono- and diterpenes are considered in this section.

Terpenes, as a rule, contain several asymmetric carbon atoms and are found naturally in an optically active form.

Monocyclic terpenes, i.e., hydrocarbons of the $C_{10}H_{16}$ composition, are unsaturated double-bonded derivatives of menthane. *Limonene*, a representative of this group of terpenes, was so called because it is in the composition of lemon oil. It is found also in the oils of other citruses (oranges and mandarins) and in the essential oils of fennel, caraway, etc. It is the most widely distributed monocyclic terpene

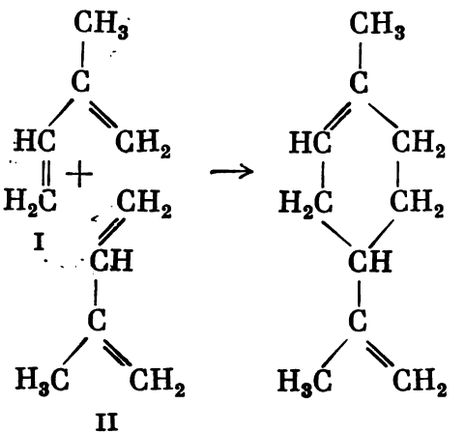
hydrocarbon.



Limonene

Limonene is a colourless liquid which boils at 176°C; it has a characteristic lemon odour and optical activity, and either a levorotatory or a dextrorotatory antipode of it is found in different essential oils.

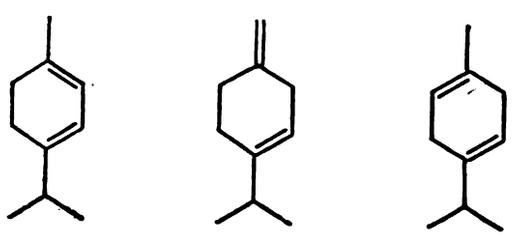
Dipentene, which is a racemic form of limonene, can be obtained when two isoprene molecules are condensed:



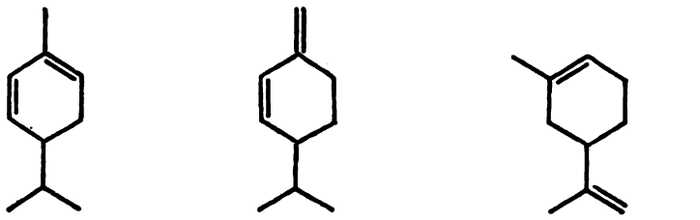
I II

This reaction is of the type of diene synthesis (p. 111), and one isoprene molecule acts as a diene (I), while another (II), as a dienophile.

The racemic form of limonene is found also in turpentine. Moreover, other monocyclic terpenes $C_{10}H_{16}$, which differ from limonene by the arrangement of double bonds, e.g., *terpinenes* and *phellandrenes*, are contained in essential oils:



α-Terpinene β-Terpinene γ-Terpinene

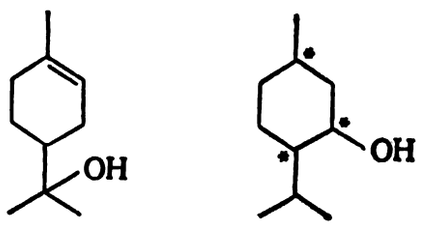


α-Phellandrene β-Phellandrene Sylvestrene

Sylvestrene, unlike other monocyclic terpenes, is a derivative of *m*-menthane.

Let us consider the most important hydroxyl derivatives of monocyclic terpene hydrocarbons.

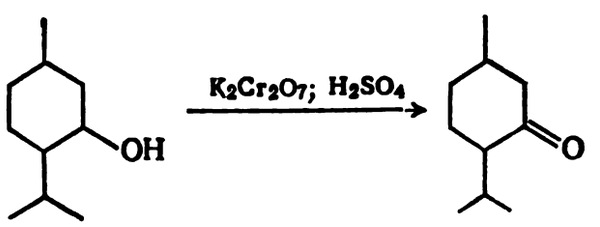
Alpha terpineol is found in diverse essential oils. It is a liquid which boils at 219°C; it has a pleasant odour, like that of lilac and lily of the valley, and is widely used in perfumery.



α-Terpineol Menthol

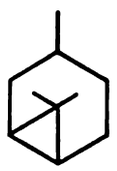
Menthol is a crystalline substance with a peculiar odour, and it is the main component of peppermint oil. It is a saturated alcohol of the cyclohexane series. It has three asymmetric carbon atoms and exists as eight stereoisomers. Menthol acts as a weak disinfectant, and it is used in medicine, for making toothpaste.

The ketone called *menthone* is formed when menthol is oxidized by the chromic-acid mixture:

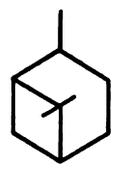


Menthone is a liquid which boils at 207°C, and its odour is similar to that of menthol. Being a ketone, it forms such derivatives as oxime, phenylhydrazone, etc. Menthone, like menthol, is found in peppermint oil.

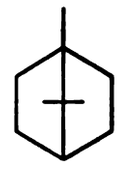
Bicyclic terpenes are derivatives of the following three isomeric hydrocarbons of the $C_{10}H_{18}$ composition (carane, pinane and bornane*):



Carane



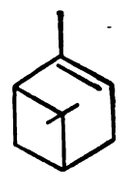
Pinane



Bornane (camphane)*

It can be imagined that these hydrocarbons originated from menthane whose isopropyl grouping "bent" into the ring, and then its central carbon atom formed a bond with one of the carbon atoms of the cyclohexane ring.

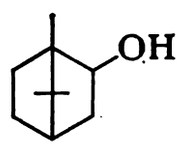
Alpha pinene, a bicyclic terpene hydrocarbon of the pinane group found most widely in nature, is a liquid which boils at 156°C.



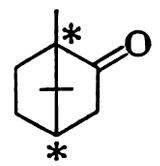
α-Pinene

It is one of the main components of turpentine, and has a pleasant pine odour. It is widely used as a solvent for making lacquers and paints. Pinene is used to obtain synthetic camphor and other compounds, and also insecticides (polychloropinene) and oils for ore flotation. When α-pinene is hydrogenated, it produces pinane, which is not found naturally.

Borneol (bornane derivative) is a widely distributed bicyclic terpene alcohol:



Borneol



Camphor

It is found in many essential oils: the dextrorotatory isomer is found in camphor, lavender and rosemary oils, and the levorotatory

* Camphane is an old name for the hydrocarbon called bornane. But it is better not to use it, because the compound called camphene has a structure which is quite different from that of camphane.

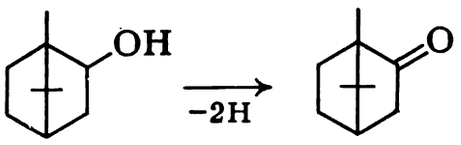
isomer, in pine oil. Borneol is a solid crystalline substance which dissolves slightly in water and readily in organic solvents. There is an extraordinarily small difference between the melting and boiling points of this alcohol (204°C and 210°C, respectively), and therefore borneol readily sublimes.

Camphor is a crystalline substance which melts at 179°C and has a peculiar odour.

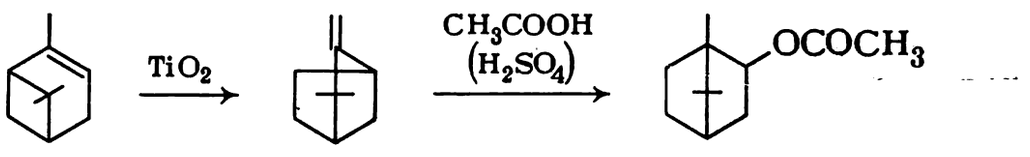
The presence of two asymmetric carbon atoms (nodal atoms which are denoted by asterisks in the formula) in the camphor molecule should, as a general rule, engender four optical isomers. But in fact only a pair of optical antipodes is known, i.e., (+)- and (—)-camphor and optically inactive (racemic) camphor. The stereoisomeric forms of camphor are numerically less, because the configurations of both asymmetric atoms are interconnected in a rigid bicyclic system. These configurations can be changed only simultaneously.

Camphor is found naturally mostly in the leaves, roots and wood of camphor laurel as (+)-camphor. The oil of camphor laurel is the source of natural camphor. It is contained in smaller amounts in other essential oils (basil, wormwood and sage oils).

Camphor is used in medicine as a means to stimulate cardiac activity, and is employed in large amounts as a plasticizer for obtaining celluloid (see p. 406). Natural sources cannot completely satisfy the requirement for camphor, and therefore it is synthesized as well. In the Soviet Union, camphor is obtained by dehydrogenating borneol, which is extracted from the essential oil of the Siberian fir, the content of it in the fir being about 40 per cent (it is found both in a free state and as acetate):



In another method, α-pinene, being the main component of turpentine, is used as a starting substance. Pinene vapours are passed over the catalyst (TiO_2), and this causes the rearrangement of its carbon skeleton with the formation of camphene. Acetic acid is added to camphene; this reaction is also accompanied by a rearrangement and yields bornyl acetate:

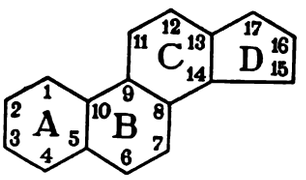


α-Pinene Camphene Bornyl acetate

Bornyl acetate is then saponified into borneol, from which camphor is obtained by oxidation (dehydrogenation).

The rearrangements of the carbon skeleton, like those given above, are a very common phenomenon in chemical transformations of bicyclic terpenes. It is these rearrangements which make that class of compounds so peculiar; owing to this property, it was very difficult to ascertain the structure of terpenes. The Russian scientist E. E. Wagner, who contributed much to terpene research, figuratively called them "chemical chameleons".

22.10. Steroids. Steroid compounds are based on the tetracyclic structure called *cyclopentaneperhydrophenanthrene*. Its scheme together with the accepted numeration is given below (it is assumed to denote nuclei by Latin letters):

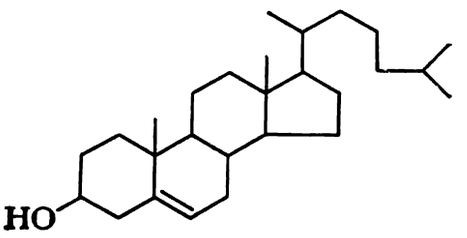


Steroids usually contain methyl groups in the positions 10 and 13, and also side chains and substituents in other sites (mostly in positions 3 and 17) and multiple bonds. All the nodal atoms of the cyclic structure (5, 8, 9, 10, 13 and 14) are asymmetric (asymmetry is also exhibited in the monosubstitution of other atoms), as a result of which steroids have a large number of stereoisomers. This as well as structural isomerism make steroid compounds very diverse.

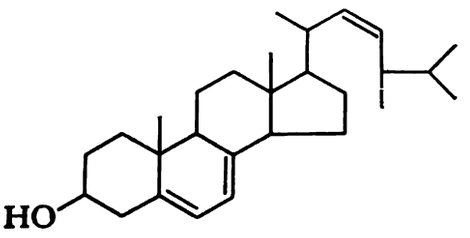
Compounds of a steroid type are widely distributed naturally. Steroids include cholesterol, a fatty substance which is contained in every cell of a living organism. Other steroids are contained in plant cells. Bile acids, toad poisons, and some poisonous substances of plants (saponins) have the steroid skeleton. Hormones, which are produced by the pancreas and sexual glands, also have a steroid nature.

Cholesterol consists of plates which feel greasy, and its melting point is 149°C. It is insoluble in water, but soluble in organic solvents. It is contained in all the tissues of animals and Man especially in the brain, liver, kidneys, and the blood. In some diseases, the amount of cholesterol in human blood deviates from the standard (160-220 mg in 100 ml). Some cholesterol enters the organism when food is eaten (especially much of it is contained in fats and the egg yolk), but it has now been ascertained that about 80 per cent of cholesterol is synthesized in the organism. Therefore, cholesterol is deposited on the walls of blood vessels in atherosclerosis mainly because its metabolism in the organism is upset, and not because too

much of it enters the organism together with food.



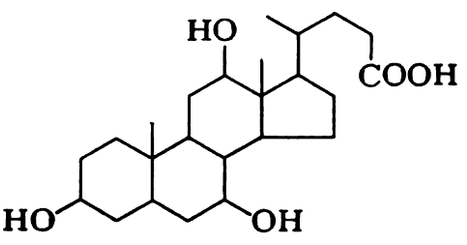
Cholesterol



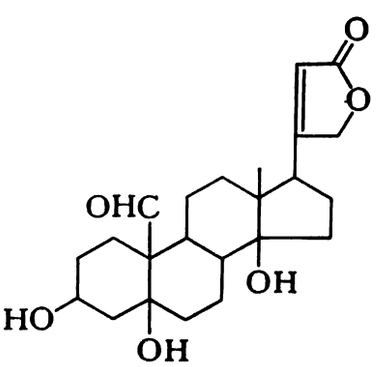
Ergosterol

Ergosterol, unlike cholesterol, has two more double bonds and one methyl group. It turns into vitamin D_2 when it is exposed to ultraviolet rays.

Cholic acid belongs to the group of *bile acids*, i.e., compounds having a steroid skeleton that are contained in bile. These substances promote the assimilation of fats, and also bind certain poisons and help to remove them from the organism.



Cholic acid



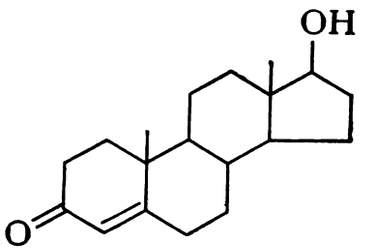
Strophanthidin

Strophanthidin is the basis of many cardiac glycosides, i.e., substances of plant origin that are strong poisons (they arrest cardiac activity). But these substances stimulate cardiac activity when they are given in small doses, and therefore they are used in medicine. Strophanthidin in combination with rhamnose carbohydrate is in the composition of *convallotoxin*, a cardiac glycoside found in lavender.

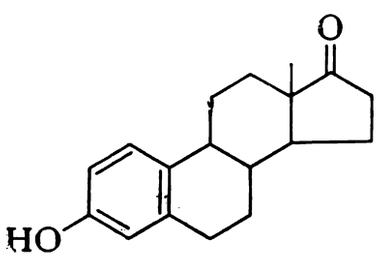
A similar structure is possessed by steroid *bufogenins*, i.e., toad poisons, and *saponins*, which are plant glycosides capable of producing, with water, very stable foam.

Hormones are substances produced by the endocrine glands; they control the most vital processes. Let us now consider some steroid hormones, although there are hormones of a polypeptide nature (insulin) and of the aromatic series (adrenaline). Steroid hormones are produced by the cortex of the adrenal glands and by sexual glands.

They control the growth of the organism and the processes of its ageing, and affect reproduction functions and many other aspects of vital activity. The formulas of male and female sex hormones are given below:

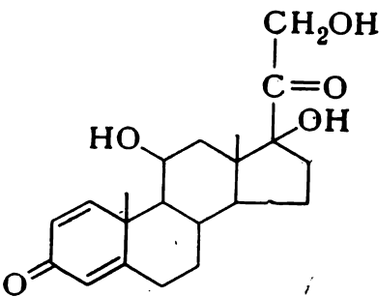


Testosterone
(male sex hormone)

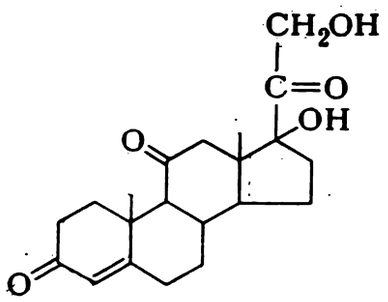


Estrone
(female sex hormone)

Cortisone is among the 20 hormones which are produced by the adrenal cortex. It controls carbohydrate metabolism and is used for treating many serious illnesses (rheumatism, bronchial asthma, inflammatory processes, and allergic diseases). Cortisone is obtained synthetically from steroid compounds which are readily available, such as cholesterol or solasodine, which is extracted from the plant called nightshade *Solanum sodomaeum*. Cortisone analogues, e.g., *prednisolone*, are also synthesized.



Prednisolone



Cortisone

Chapter 23

HIGH-MOLECULAR-WEIGHT COMPOUNDS

23.1. Classification. Connection Between Structure and Properties. In the preceding chapters, we frequently mentioned various organic compounds whose molecules are very large; they include rubber, proteins and polysaccharides. Such compounds, whose molecular mass ranges from several thousands to millions, have become known as *high-molecular-weight compounds* (*polymers*). As we have already seen, some of them perform important functions in living organisms. Many diverse high-molecular-weight compounds used for making different materials, such as plastics, fibres and elastomers, are now synthesized. It is very important for these materials to possess good *physico-mechanical properties*, i.e., strength, elasticity, thermostability, etc. A study of high-molecular-weight compounds has shown that their physico-mechanical properties depend especially on the *shape of molecules.*

The shape of molecules is used in distinguishing two extreme types of polymers from one another: linear (thread-like) and three-dimensional (bulky, globular) ones. There are also many polymers which hold an intermediate position between these extreme types.

Linear polymers are characterized by their ability to form strong fibres and films, and by considerably great elasticity and the ability to dissolve and, at elevated temperature, melt. Typical representatives of linear polymers are rubber, and its synthetic analogues, polyamide fibres.

Three-dimensional polymers do not melt and are insoluble; they are far less elastic than linear polymers, and are often also brittle. Generally speaking, the conceptions of "molecule" and "molecular mass" are meaningless for such polymers, because every object made out of a three-dimensional polymer is a gigantic molecule. The term "cross-linked polymers", which is sometimes used for them, suggests that linear polymers can be made into three-dimensional ones by "cross-linking" chain macromolecules in a three-dimensional network. It is this process which occurs when rubber is vulcanized. Other typical representatives of three-dimensional polymers are phenol-formaldehyde and glyptal resins.

Of course, the physico-mechanical properties of a polymeric material are affected not only by the shape, but also by the *chemical*

nature of a macromolecule. If there is no considerably great interaction between macromolecules of a linear polymer (this means that there are no strongly interacting polar groups in the macromolecule), macromolecules can easily move relative to one another, and the corresponding material turns out to be elastic. This is true of nonvulcanized rubber and polyethylene (especially on heating). But the elasticity of such materials is limited. As the interaction between macromolecules of a linear polymer grows (i.e., as interacting polar groups accumulate i the polymer), its properties gradually become similar to those of a three-dimensional polymer. This applies to cellulose, whose linear macromolecules are strongly linked together by hydrogen bonds. The same result can be obtained by chemically "cross-linking" linear macromolecules.

There are *carbochain* (the polymeric chain consists of only carbon atoms) and *heterochain* (the polymeric chain has atoms of different elements in its composition) polymers, depending on the composition of the main chain. *Organoelement* polymers constitute an important class; besides ordinary organogen elements, they include atoms of other elements, i.e., silicon, phosphorus, boron, titanium, etc.

High-molecular-weight compounds originate when many mole cules of low-molecular-weight substances, or monomers, combin with one another. This can be effected by polymerization or polycon densation. Polymers are divided into polymerization and polycondensation ones, depending on the methods of obtaining them.

POLYMERIZATION HIGH-MOLECULAR-WEIGHT COMPOUNDS

23.2. Polymerization Reactions. Polymerization reactions consist in the addition of many monomeric molecules to one another. They can be conventionally represented by the following scheme:

$$n\mathrm{M} \longrightarrow \mathrm{M}_n$$

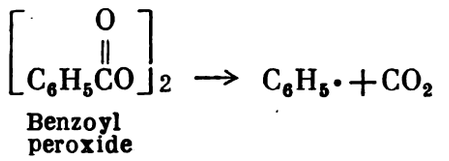
where M = monomeric molecule;
M_n = polymeric molecule (macromolecule);
n = number of monomeric units in a macromolecule (degree of polymerization).

Polymerization reactions occur due to addition to multiple bonds or to the opening of cycles. To this end, it is enough for a monomer to have one reactive grouping.

An *initiator* gives an impetus to a chain reaction. Substances which readily decompose into free radicals often act as initiators. Such a radical transforms a monomeric molecule into a radical form and thus gives an impetus to a chain polymerization reaction (*radical*

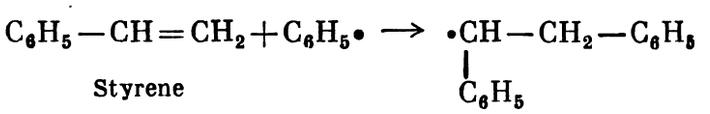
polymerization). For example, styrene turns into polystyrene under the action of benzoyl peroxide.

Initiation step:



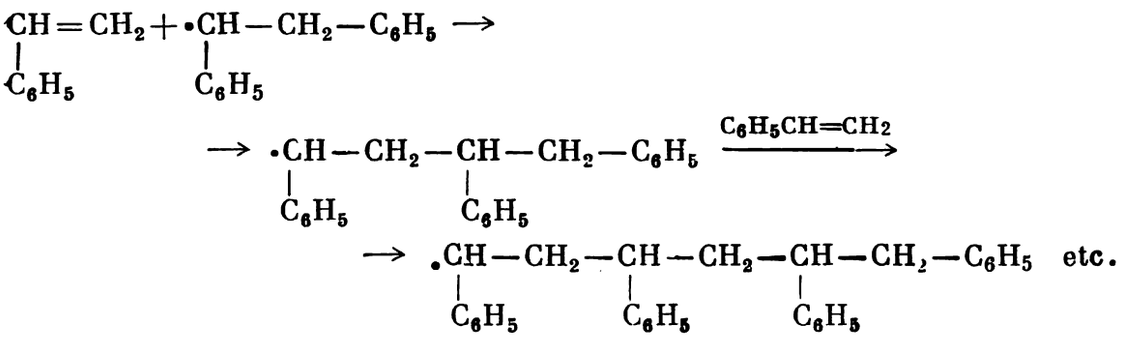
Benzoyl peroxide

The first step of the chain propagation:



Styrene

Chain propagation:



Chain polymerization occurs at a rapid rate even at low temperature. The polymerization rate is sometimes so high that the reaction occurs explosively. Intermediate polymerization products are unstable particles. In our case, they are radicals, but they can also be ions. After the primary initiation of the reaction, the chain will grow until the entire monomer is depleted or the chain is terminated.

Besides radical polymerization reactions, there are polymerization reactions which occur by the *ionic mechanism*, i.e., their active particles can be either positive (cationic polymerization) or negative (anionic polymerization) ions.

Monomers, which are polymerized by one of the mechanisms, can be inert in polymerization by another mechanism. For example, styrene undergoes cationic, and not anionic, polymerization. Conversely, methyl methacrylate is polymerized by the anionic, and not the cationic, mechanism. Both monomers have approximately the same activity in radical polymerization.

Besides chain polymerization, there is also stepwise polymerization. An example of it is the polymerization of isobutylene in the presence of sulphuric acid (see p. 90).

If two or more structurally different monomers are included in a polymer chain, the polymer is called a *copolymer* and the polymerization reaction is known as *copolymerizaton*. The properties of the materials being obtained can be precisely controlled by changing the mixture of monomers; examples of this will be given further.

23,3. Polyolefins. Olefin polymerization, in which valuable high-molecular-weight materials are formed, is especially important now.

The first observations of olefin "consolidation" were made by A. M. Butlerov. In particular, he described how the isobutylene dimer is obtained and noted that this process can occur further with the addition of the third and subsequent molecules. But olefins were polymerized with the formation of solid polymeric products much later, i.e., only in the 1940's and 1950's.

The simplest olefin, ethylene, can be polymerized by different methods, i.e., it can be polymerized under a pressure of 1200-1500 kg/cm^2 by initiating polymerization by oxygen or organic peroxides (*high-pressure polyethylene*), or under low pressure on organometallic catalysts which are mixtures of aluminium alkyls and titanium salts (*low-pressure polyethylene*):

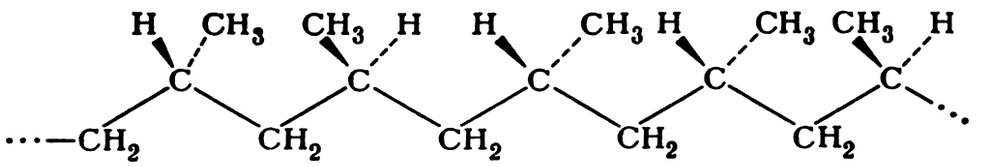
$$CH_2=CH_2 \longrightarrow \ldots-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\ldots$$

Polyethylene is essentially a saturated hydrocarbon whose molecular mass ranges from 20,000 to one million. It is a transparent material with high chemical stability; its softening point is 100-130°C, its tensile strength is 120-340 kg/cm^2, and its thermal and electric conductances are low. Polyethylene is used for insulating electric wires and making transparent films. These films are used as packing material and as a covering for plants in hot-houses instead of glass. Dishes and other articles are also made out of polyethylene.

Polypropylene is obtained from propylene similarly as polyethylene. It was long believed that only oil-like products can be obtained in propylene polymerization. When the techniques of *stereospecifically polymerizing* (see further) propylene were mastered, it turned out that a transparent material, which has a softening point of 160-170°C, a tensile strength of 260-500 kg/cm^2 and good electric-insulation properties, is obtained in this case. Polypropylene threads are obtained by pressing the propylene melt through spinnerettes. Polypropylene fibre has great strength and high chemical stability. It is used to make cables, fishing nets, and filter cloth. The fibre is not used much in the textile industry, because it is not susceptible to ordinary dyes. But now there are dyes which colour this polymer in bulk.

The stereospecific polymerization of propylene consists in creating a strictly ordered three-dimensional structure of a linear polymeric chain. In polymerization, *asymmetric carbon atoms* originate in a polymeric chain. Their configuration can alternate disorderly, and

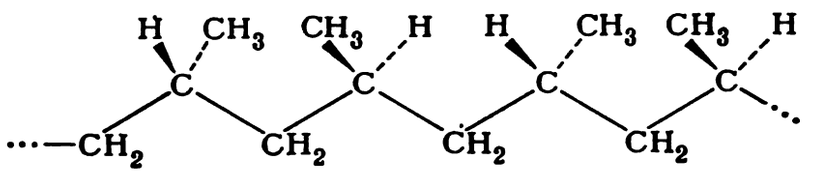
the product of this is called *atactic polypropylene*:



A

In formula A, the main chain of macromolecules (alternating groups of $-CH_2-\overset{|}{\underset{|}{C}}-$) is conventionally represented as lying on the paper plane*, while hydrogen and the CH_3 group must be imagined as protruding from both sides of this plane. In atactic polypropylene, the CH_3 groups and the hydrogen atoms are arranged "below" (dotted line) and "above" (bold line) the plane without any regularity.

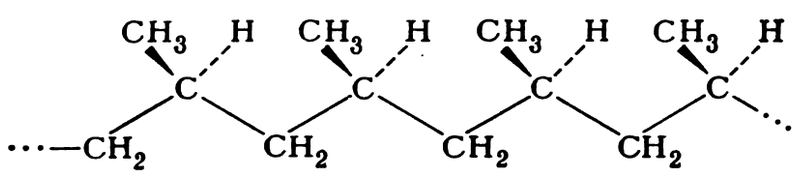
Ordered three-dimensional structures, particularly the *syndiotactic polymer* B, whose three-dimensional structure is given below, originate in stereospecific polymerization:



B

The syndiotactic polymer is characterized by a regular alternation of the three-dimensional arrangement of the substituents H and CH_3: each group is on the same side of the drawing in every other unit.

In the *isotactic polymer* C, all the same groups (CH_3) are on one side of the drawing ("toward us"), while all the H atoms are on the other ("away from us"):

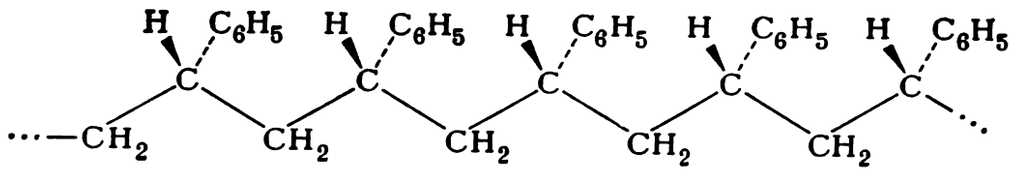


C

Isotactic stereoregular polymers are the ones which possess the most valuable physico-mechanical properties.

* This is not quite correct, because the main chain forms a three-dimensional helix.

Isotactic polymers are obtained from styrene as well. The structure of isotactic polystyrene is given below:

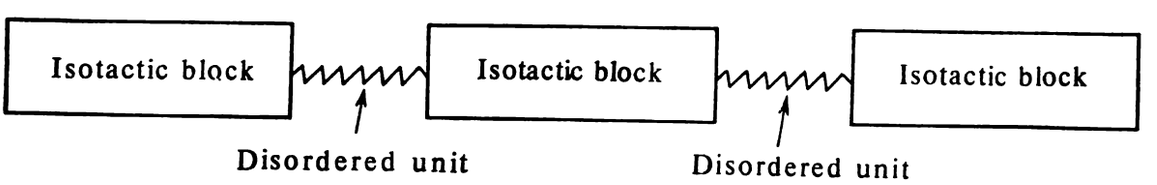


Polystyrene, a colourless transparent material, is commonly used for making various plastic glass articles. The softening point of atactic polystyrene is ca. 85°C, while that of isotactic polystyrene is 230°C, and therefore the latter can be employed at higher temperatures. Wide use is also made of the copolymers of styrene with other monomers, such as acrylonitrile I, methyl methacrylate II and α-methylstyrene III:

$$\underset{\text{I}}{CH_2=CH-CN} \qquad \underset{\text{II}}{CH_2=C(CH_3)-COOCH_3}$$

$$\underset{\text{III}}{C_6H_5-C(CH_3)=CH_2}$$

Copolymers have higher physico-mechanical indices than pure polystyrene. Especially valuable shock-proof polystyrene is obtained by *block copolymerization*, as a result of which regions (blocks), of two different polymers are originated. *Stereoblock polymerization* can be used to obtain the same results without employing a mixture of monomers: the stereoblock polymer originates from one monomer, while blocks in this case are regions which differ from one another not by their composition, but by their three-dimensional structure. A diagram of a stereoblock polymer, which consists of isotactic blocks that are divided by regions of a chain having a disordered three-dimensional structure, is given below:



Polymeric properties can change, depending on the length of blocks and the frequency and size of disordered regions. A polymer is strong when its regions are ordered and crystalline, and it is elastic when they are disordered and amorphous. To obtain a material with the necessary properties, it is necessary to create the corresponding relationship between the crystalline and amorphous parts. An interesting

fact is that this is also true of metals: their strength and elasticity likewise depend on the degree of crystallinity.

23.4. Vinyl Polymers. Besides hydrocarbons, there are many other double-bonded compounds which are capable of being polymerized; they are known as *vinyl monomers*. Their general formula is $CH_2=CH-X$, where X is Cl, CN, $COOCH_3$, etc. The formula for polymers being obtained is given below:

$$\ldots-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-\ldots$$

Among polymers of this type, polyvinyl chloride (X is Cl) is especially important. It began to be produced in the late 1930's, and it was the most greatly produced synthetic material until 1965. Polyethylene is now manufactured in the greatest amount, but polyvinyl chloride is still produced in large amounts, i.e., it accounts for about 20 per cent of the entire output of synthetic materials.

Polyvinyl chloride is a strong thermoplastic material, whose molecular mass is 300,000-400,000. It is solid at room temperature, but it can be made soft and elastic by mixing it with sparingly volatile solvents, which are known as *plasticizers*, i.e., such as dibutyl and dioctyl phthalates and tricresyl phosphate. Plasticized polyvinyl chloride is used to make flexible sheets (for covering the floor and walls) and films, and for moulding various articles under pressure and producing artificial leather and protective gloves. Rigid unplasticized polyvinyl chloride is used to make pipes (they are not corroded, and are employed instead of lead pipes when chemical devices are being made), and door and window parts. In electrical engineering, polyvinyl chloride is used for insulating wire and making apparatus parts. It is employed also for making toys, sports equipment, stationery, and upholstering materials. Moreover, fibres can be obtained from polyvinyl chloride. It is one of the cheapest types of synthetic fibre, and is used for making filter cloth for technological processes, fishing nets, knitwear and linen used in medicine (polyvinyl chloride fibre). When polyvinyl chloride is subjected to special treatment, it can be made into a porous sponge-like material called polyvinyl chloride foam. It is used for making artificial leather, rug backing and floor covering.

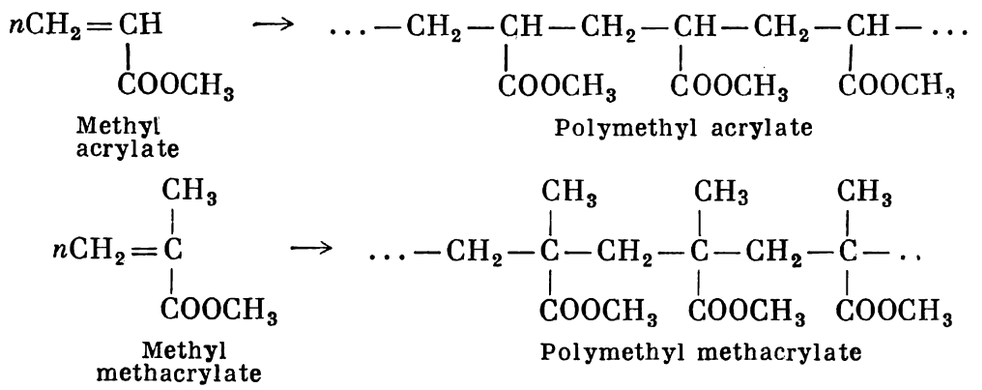
Polymers made out of *fluorinated ethylenes*, i.e., polychlorotrifluoroethylene out of chlorotrifluoroethylene and polytetrafluoroethylene out of tetrafluoroethylene, are of great importance, owing to their thermal and chemical stability:

$$n CF_2=CClF \longrightarrow \underset{\text{Polychlorotrifluoroethylene (Fluoroplast-3)}}{\ldots-CF_2-CClF-CF_2-CClF-\ldots}$$

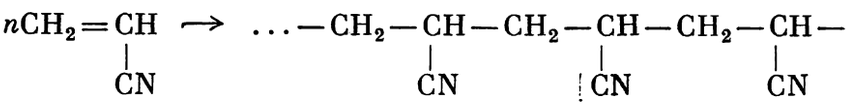
$$n CF_2=CF_2 \longrightarrow \underset{\text{Polytetrafluoroethylene (Teflon, Fluoroplast-4)}}{\ldots-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-\ldots}$$

Polyfluoroethylene resins are similar to noble metals by their chemical inertness: they are not affected by concentrated acids, oxidizing agents, aqueous alkaline solutions and ordinary organic solvents. They can be used at 250-300°C. These polymers are of great importance in many fields of new technical devices.

Wide use is made of *polymethyl acrylate* and *polymethyl methacrylate*, which are obtained from the esters of unsaturated acids, i.e., acrylic and methacrylic acids. These monomers also relate to vinyl monomers. Plexiglas, a transparent polymer, is obtained from them:

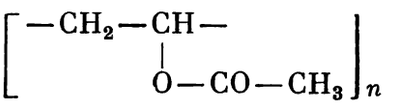


Valuable materials are obtained in acrylonitrile polymerization:



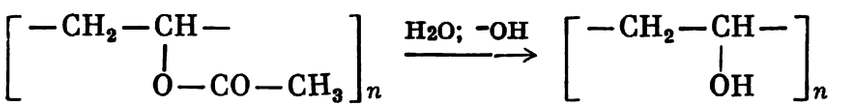
The fibre called Nitron (also Orlon, Acrilan), or artificial wool, is made out of polyacrylonitrile. These fibres can be obtained by *dry spinning*, i.e., by pressing a solution of polyacrylonitrile in dimethyl formamide, which is heated to 120-130°C, through spinnerettes into a shaft which has hot air (180-250°C). The solvent is evaporated and thread is formed in it. But *wet spinning* is a more commonly used method; by this method, the polymer solution passes through spinnerettes and enters a settling bath (a mixture of a solvent and water). The yarn obtained is used for making knitwear and suits, industrial textiles.

Monomers include ethers and esters of vinyl alcohol (see Secs. 10.14 and 12.19), e.g., vinyl acetate, which gives a polymer of the following structure:



Polyvinyl acetate is used for making lacquers and glues, and for impregnating textiles to make them crease-resistant. *Polyvinyl alcohol* is obtained when polyvinyl acetate is hydrolyzed in the pres-

ence of a small amount of alkali:



Polyvinyl alcohol (Vinnol), unlike other polymers, is readily soluble in water due to the presence of hydroxyl groups, but is insoluble in hydrocarbon organic solvents. It is used for obtaining the synthetic fibre called Vinol. Owing to the presence of free hydroxyl groups, residues of different carboxylic acids can be introduced into this fibre, thus imparting ion-exchange, bactericide and other indispensable properties to the *modified polymer* which is obtained. A valuable property of the Vinol fibre is its hygroscopicity, while films made out of polyvinyl alcohol are characterized by low gas permeability.

23.5. Rubber, Natural and Synthetic. Natural rubber, or caoutchouc, is an elastic amorphous mass which is obtained from the *latex* of rubber plants. The best known rubber plant is *Hevea braziliensis*, which is native to the Brazilian jungle.

Smaller amounts of natural rubber are contained in several other plants, mainly tropical ones. Specimens of natural rubber were brought to Europe in the eighteenth century, but there was no special utilization of it. It was only in 1823 that Macintosh, a Scot, discovered a way of impregnating textiles with rubber and began to make raincoats; such a raincoat is called after him even now. The raincoats were not of high quality: in warm weather, rubber which impregnated them became sticky, while in winter, it became hard and brittle.

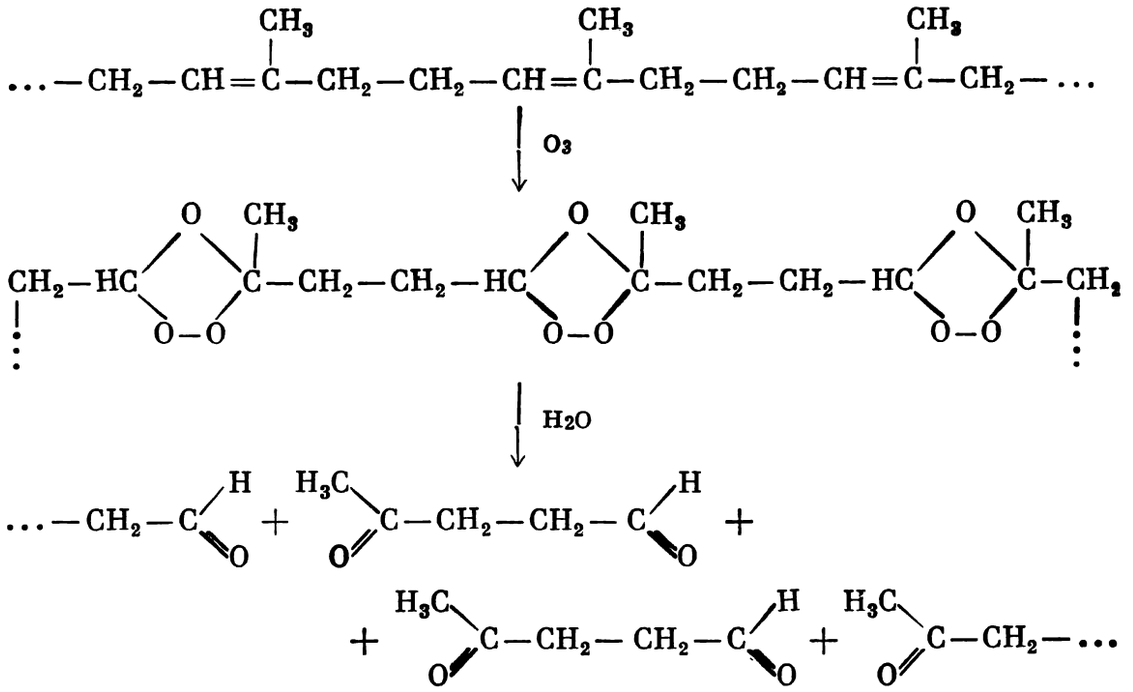
Natural rubber began to be used industrially in 1839, when the method of turning it by sulphur treatment (vulcanization) into *rubber*, a material whose especially valuable property is elasticity, was mastered. Since then, rubber began to be used on a rapidly growing scale. Soon, the automobile industry began to consume it in the greatest amount, being followed by the electric-engineering industry and factories producing various rubber articles for technical purposes.

A study of the chemical properties of rubber has shown that it is a typical unsaturated compound: it adds bromine and hydrogen bromide, and undergoes catalytic hydrogenation. In dry distillation, i.e., in heating without aeration, rubber disintegrates with the formation of the diene hydrocarbon called isoprene (2-methyl-1,3-butadiene).

The basis of the modern conceptions of the structure of rubber was laid by C. Harries (1909-1912), who used the *ozonolysis reaction* for this purpose. Since then, this reaction has often been used by chemists for studying unsaturated compounds.

By ozonizing rubber, Harries obtained levulinic aldehyde, $CH_3—CO—CH_2—CH_2—CHO$. This proves that rubber is a linear

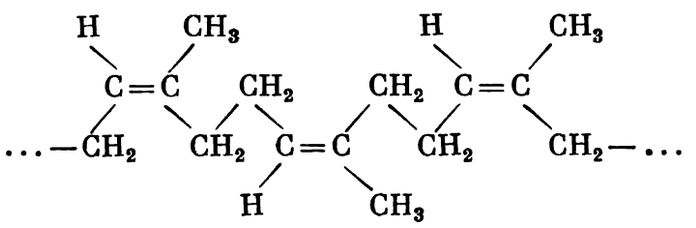
polymer in which isoprene molecules are linked together by the scheme of 1,4-addition:



Natural rubber is a mixture of *polymer homologues*, which are molecules with different molecular masses (in the 50,000-3,000,000 range). The bulk consists of fractions having a molecular mass of over one million.

It was known as early as the end of the nineteenth century that isoprene can be polymerized under the action of ultraviolet rays and chemical reagents. Of course, many attempts were made to reproduce natural rubber by isoprene polymerization. But these attempts failed for decades. The reason why they failed was discovered only after all the details of rubber structure were elucidated.

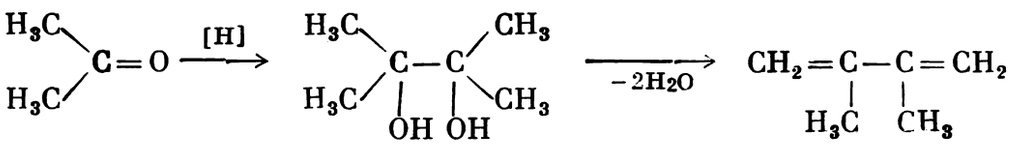
Natural rubber is a linear isoprene polymer which has not only a strictly regular structure, but also a definite configuration at the double bond. Natural rubber has a structure of 1,4-polyisoprene with a *cis*-configuration of the polymeric chain:



It is difficult to reproduce natural rubber, because this strictly regular (without any branchings) chain of the *cis*-configuration must be built synthetically.

As we have already seen, the obvious link between isoprene and natural rubber gave rise to many attempts to obtain natural rubber by isoprene polymerization. A caoutchouc-like mass was first obtained from isoprene by the scientists I. I. Ostromyslensky and S. V. Lebedev (1906). But the quality of the polymeric material which they obtained was unsatisfactory. Moreover, another difficulty evidently had to be overcome even if material of good quality were produced: at the time, it was not known yet how to produce inexpensive isoprene in large amounts. Therefore, researchers began to study the polymerization of dienes, which were more easily available.

As early as the beginning of this century, I. O. Kondakov ascertained that the isoprene homologue, 2,3-dimethyl-1,3-butadiene, is capable of giving a rubber-like mass in polymerization. Kondakov's discovery was used by Germany during World War I; 2,3-dimethyl-1,3-butadiene was obtained from acetone:



Acetone — Pinacol — 2,3-Dimethyl-1,3-butadiene

"Methyl rubber" obtained in polymerization was of inferior quality. Tyres made out of it were good only for 3000 km, while those made out of natural rubber could be used for 16,000 km; the inner tubes became useless after a few hundred kilometres. The production of this type of synthetic rubber was stopped immediately after it became less needed in warfare.

In the Soviet Union, S. V. Lebedev carried out investigations in diene hydrocarbon polymerization. In 1926, the Supreme Soviet of the National Economy of the USSR announced an international competition in working out a method of obtaining synthetic rubber; after almost two years' hard work, a group of chemists under Lebedev's guidance presented two kilograms of synthetic rubber and a description of the method of obtaining it to the jurors in accordance with the terms.

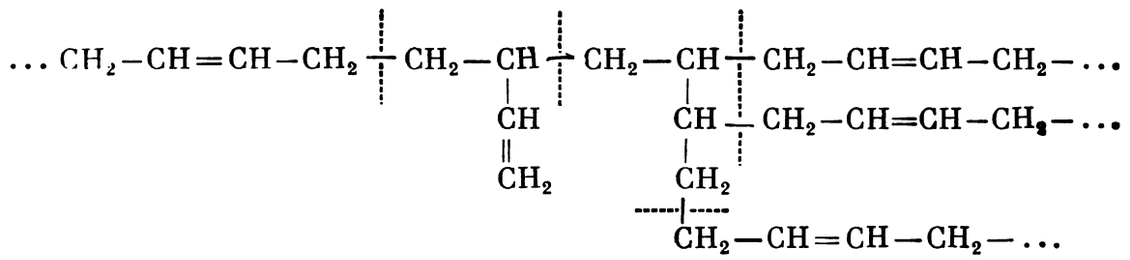
At the competition, Lebedev's work won first and only prize. It was decided to use his method as the basis for projecting the world's first large-scale production of synthetic rubber. As early as 1931, the initial 260 kg of synthetic rubber were obtained at an experimental factory, and a year later two more synthetic-rubber factories were put into operation.

Ethyl alcohol serves as raw material for obtaining synthetic rubber by Lebedev's method. It is simultaneously dehydrated and dehydrogenated with the formation of butadiene under the action of Lebedev's catalyst (a mixture of oxides of aluminium, zinc and some

other metals):

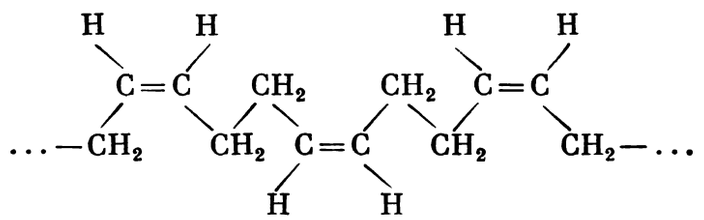
$$2C_6H_5OH \longrightarrow CH_2=CH-CH=CH_2+2H_2O+H_2$$

Butadiene is then stripped of unreacted ethyl alcohol and many by-products, and is subjected to polymerization under the action of metallic sodium. Polymerization occurs not only in the 1,4-positions, but also in the 1,2-positions, and therefore a branched macromolecule instead of a strictly linear one is obtained:



The monomeric units of butadiene in the formula above are separated from one another by dots.

Stereospecific (i.e., that which leads to a strictly regular three-dimensional form) 1,4-polymerization of butadiene under the action of organometallic catalysts was mastered only after World War II. This made it possible to considerably improve the quality of synthetic butadiene rubber. Stereoregular butadiene rubber, like natural isoprene rubber, has a polymer chain of the *cis*-configuration:



The raw material basis of the synthetic-rubber industry has also changed now. Instead of using raw food material (grain, potato) for producing the starting ethyl alcohol, it is synthesized from ethylene or obtained from wood hydrolysis products. The direct transition from butane and butylene (gases from oil cracking) to butadiene by dehydrogenation is also being used on a wider scale.

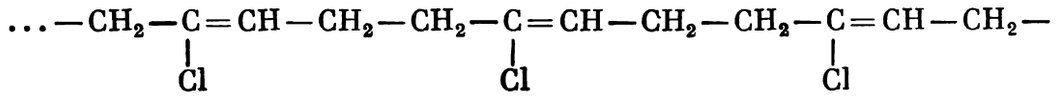
In countries which do not have petroleum, e.g., Germany, butadiene began to be produced on the basis of coal through acetaldehyde or 1,4-butynediol.

Synthetic butadiene rubber was the first rubber produced on a large industrial scale in many countries. As we have already seen, the first factories in this respect were built in the Soviet Union (1932), while in 1937-1940, synthetic butadiene rubber began to be produced in Germany and the United States. This type of synthetic rubber has lost none of its importance even today (especially as a stereoregular polymer) but other types of synthetic rubber are also being produced

now. This is especially true of the copolymers of butadiene with other monomers, such as styrene, acrylonitrile and methyl vinyl pyridine.

Stereoregular isoprene rubber, which completely reproduces natural rubber by its structure and properties, is being manufactured on a rapidly growing scale. Isoprene, which is needed for this purpose, is being obtained by catalytically dehydrogenating isopentane and by other methods.

Synthetic chloroprene rubber, which is obtained from acetylene, is also important industrially. Chloroprene is similar to isoprene structurally, but it has chlorine instead of the methyl group. Chloroprene polymerization in the 1,4-positions gives a polymer of the following structure:



The molecular mass of chloroprene rubber is more than 100,000. Articles made out of this material are better than those made out of natural rubber, because they are more stable thermally and more resistant to light and the action of oil products. Moreover, chloroprene rubber is incombustible (it contains about 40 per cent of chlorine).

Many diverse types of synthetic rubber are now being produced. Therefore, especially valuable materials which best suit their purpose can be obtained. S. V. Lebedev's prediction is coming true; he said: "Plant rubbers are essentially isoprene rubber, regardless of the rubber tree from which they are obtained. Therefore, being the bearers of a definite scale of properties, they cannot give a wide variety of properties to industry. Rubber synthesis is a source of endless diversity. But since every new rubber is the bearer of its own unique scale of properties, the rubber industry... will have great freedom, which it does not have now, in selecting the necessary properties."

As a result of the aspiration to obtain rubbers having different properties, the world production of synthetic rubbers became practically equal to the extraction of natural rubber (1.9 million and 2.0 million tons, respectively) as early as 1960. From 1963 to 1973, the output of synthetic rubber increased 2.5 times, and now over 70 per cent of all rubber is synthetic rubber.

The properties of different synthetic rubbers are given in Table 23.1.

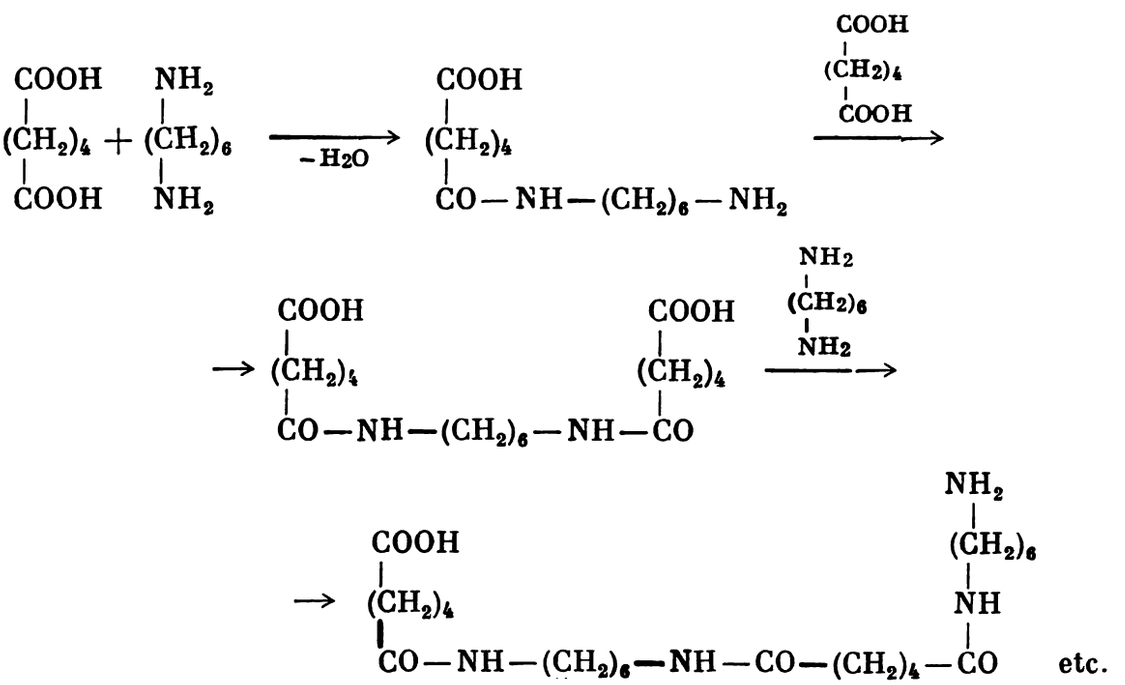
In the first decades of this century, rubber was, in a way, indispensable for motor vehicles, aviation, electric and radio engineering, and the production of various household articles. But it has now lost its monopoly; there are other synthetic polymers which have successfully replaced rubber in many fields.

TABLE 23.1. **Some Rubber Properties**

Type of synthetic rubber	Composition	Properties of rubbers with active fillers (soot)		
		temperature limits of utilization, °C	tensile strength, kg/cm²	specific elongation, %
Sodium butadiene	Butadiene	from —52 to +150	100-150	350-450
Stereoregular butadiene	Butadiene	from —110 to +150	160-190	400-600
Styrene butadiene	Butadiene (72%), styrene (28%)	from —68 to +150	200-250	550-650
Nitrile butadiene	Butadiene (74%), acrylonitrile (26%)	from —47 to +160	250-280	600-700
Stereoregular isoprene	Isoprene	from —110 to +150	200-300	600-800
Natural	Isoprene	from —71 to +150	250-350	600-850
Chloroprene	Chloroprene	from —57 to +170	200-300	600-700

POLYCONDENSATION HIGH-MOLECULAR-WEIGHT COMPOUNDS

23.6. Polycondensation. Usually bifunctional monomers participate in these reactions; their molecules are added to one another with the loss of a simple molecule (usually water). A classical example is polycondensation of adipic acid with hexamethylenediamine, which gives the polyamide called nylon 66:



The condensation polymerization process occurs stepwise, i.e., one molecule is added to another. All the intermediate products are stable compounds which must be activated every time for further addition. They are activated by heating. In the polycondensation polymerization process, the molecular mass of a polymer gradually grows.

Besides the two main ways of synthesizing high-molecular-weight compounds, i.e., polycondensation and polymerization, another technique, called *addition polymerization*, is now becoming important. For instance, addition polymerization is used to obtain polyurethane rubber, which is a valuable material. In this case, the monomers are diisocyanates and glycols, which react according to the following scheme:

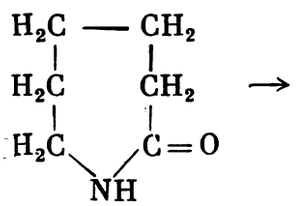
$$O=C=N-(CH_2)_n-N=C=O+HO-(CH_2)_m-OH \longrightarrow$$
$$\longrightarrow \ldots-O-(CH_2)_m-O-CO-NH-(CH_2)_n-NH-CO-O-(CH_2)_m-O-\ldots$$

23.7. Polyamides. These high-molecular-weight compounds, in which the monomeric units are linked by the groups —CO—NH—, constitute an important group of synthetic materials. Polyamides are structurally related to proteins (see Sec. 22.2). Raw material for obtaining polyamides is not as easily available as simple vinyl monomers, and therefore polyamides are more expensive. However, they are produced in large amounts owing to their exceptionally valuable physicomechanical properties. They are used mainly for making synthetic fibres. These polymers are obtained by *polycondensation*. A polymer is obtained from adipic acid and hexamethylenediamine:

$$\ldots-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-\ldots$$

A fibre is obtained when the melt of this polymer is pressed through spinnerettes at 280°C. It is known as *anid* in the Soviet Union, *nylon 66* in the United States, *perlon T* in West Germany, and *luron* in Britain.

Caprolactam is the original substance for obtaining the polyamide fibre called *capron* in the Soviet Union, *nylon* 6 in the United States, *perlon* in West Germany, *dederon* in the German Democratic Republic, *silon* in Czechoslovakia, and *grilon* in Switzerland:



$$\longrightarrow \ldots-NH-(CH_2)_5-CO-NH-(CH_2)_5-CO-NH-(CH_2)_5-CO-\ldots$$

A related fibre called *enanth* is obtained by polycondensing ω-aminoenanthic acid. It has the following structure:

$$\ldots\text{—NH—}(CH_2)_6\text{—CO—NH—}(CH_2)_6\text{—CO—NH—}(CH_2)_6\text{—CO—}\ldots$$

Initial monomeric acid is synthesized from ethylene and carbon tetrachloride (telomerization reaction):

$$3CH_2{=}CH_2 + CCl_4 \longrightarrow$$

$$\longrightarrow Cl\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CCl_3 \xrightarrow{NH_3}$$

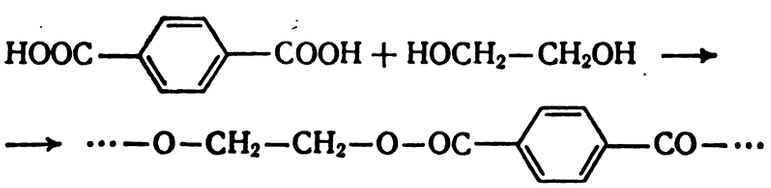
$$\longrightarrow H_2N\text{—}(CH_2)_6\text{—}CCl_3 \xrightarrow{H_2O} H_2N\text{—}(CH_2)_6\text{—}COOH$$

Polymers are obtained also from other aminocarboxylic acids which contain 11 and 12 carbon atoms.

Polyamide fibres are very strong (their tensile strength reaches 4000 kg/cm^2), and they remain almost as strong even in a moist state; moreover, they are very elastic and highly resist the action of many chemical reagents and microorganisms. These fibres undergo dyeing well. Polyamide fibres are used for household textiles, and are also important in the technological field: they are used to make parachutes, the carcasses of high-strength tyres for motor-cars and planes, and conveyer belts. Fishing nets and filter cloths are also made out of polyamide fibres

To make polyamide fibres more resistant to the action of light and atmospheric oxygen, they are stabilized by the salts of some metals and aromatic amines. *Optical bleaching agents*, i.e., substances which absorb ultraviolet light and transform it into blue light, are introduced in order to inhance the whiteness of the fibres.

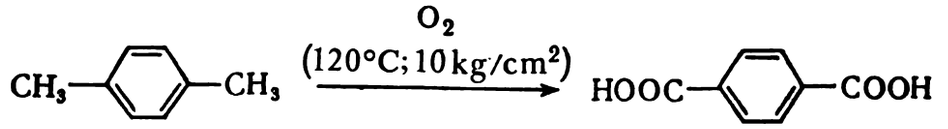
23.8. Polyesters. High-molecular-weight materials of a polyester type are obtained by polycondensing dicarboxylic acids with polyhydric alcohols. An example is *polyethylene terephthalate*, which is a high-molecular-weight ester of ethylene glycol and terephthalic acid:



Instead of terephthalic acid, its dimethyl ester can be used.

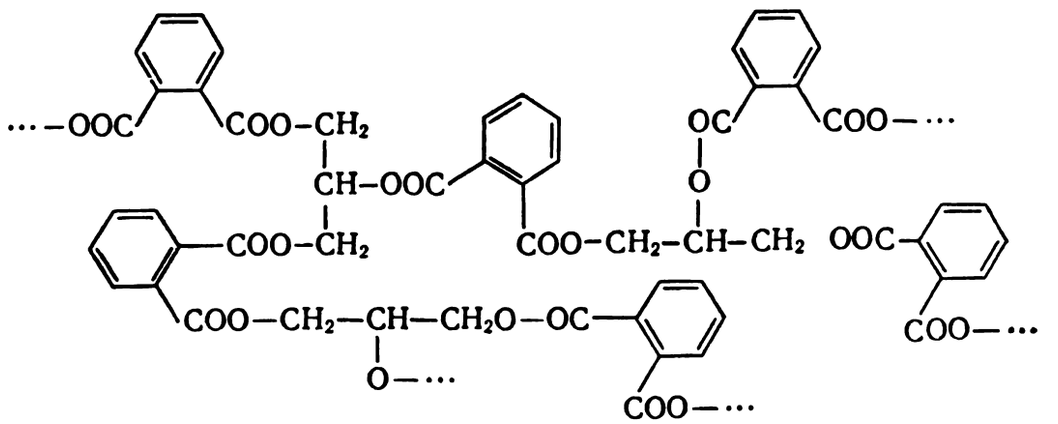
Polyethylene terephthalate is used for making films and fibres. Its commercial name is *lavsan* in the Soviet Union, *terylene* in Britain, and *Dacron* in the United States. It is used in a mixture of cotton, wool and other fibres to make textiles and knitwear. Polyester fibres, which appeared at the market later than polyamides, now lead all other synthetic fibres by their growth rates. Lavsan production is

economical solely because terephthalic acid is cheap. It is now produced with a high yield (97-98 per cent) and the required degree of purity (up to 99.9999 per cent) by catalytically oxidizing *p*-xylene (the catalyst is a solution of manganese salt in acetic acid):



Lavsan is valuable, because it is strong, chemically stable, and does not shrink or stretch (it is used for making men's noniron shirts).

Polyesters are *glyptal resins*, which are obtained when glycerol and phthalic acid are polycondensed. The presence of three hydroxyl groups in the glycerol molecule creates conditions for building a *three-dimensional* polymer:

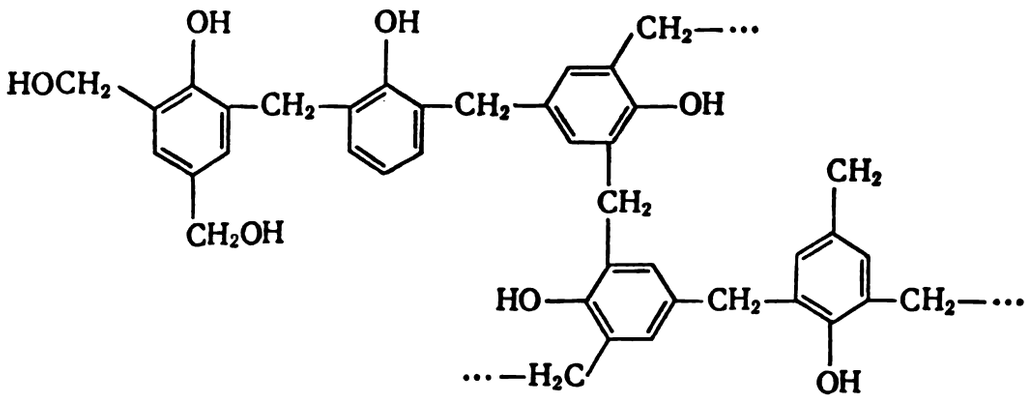


Instead of glycerol, pentaerythrite, $C(CH_2OH)_4$ (*pentaphthalic resins*), can be used. Saturated and unsaturated fatty acids are also introduced together with phthalic acid. Glyptal, pentaphthalic resins and the products of their modification by diverse additives are commonly known as *alkyd resins*. They are dissolved in different organic solvents (aliphatic or aromatic hydrocarbons); dyes are then added, and *enamels* and *lacquers* for painting coaches, machine-tools and farm machinery are obtained. Alkyd resins are used also for making printer's ink, linoleum and glue. When these resins become dry, they produce firm films, and this is important for the foregoing purposes.

23.9. Phenol-formaldehyde Resins. The artificial material obtained by polycondensing phenol with formaldehyde was the first plastic obtained as early as the nineteenth century, but it has lost none of its importance even today. This material became known as *bakelite* after the name of its inventor, a Briton called Baekeland.

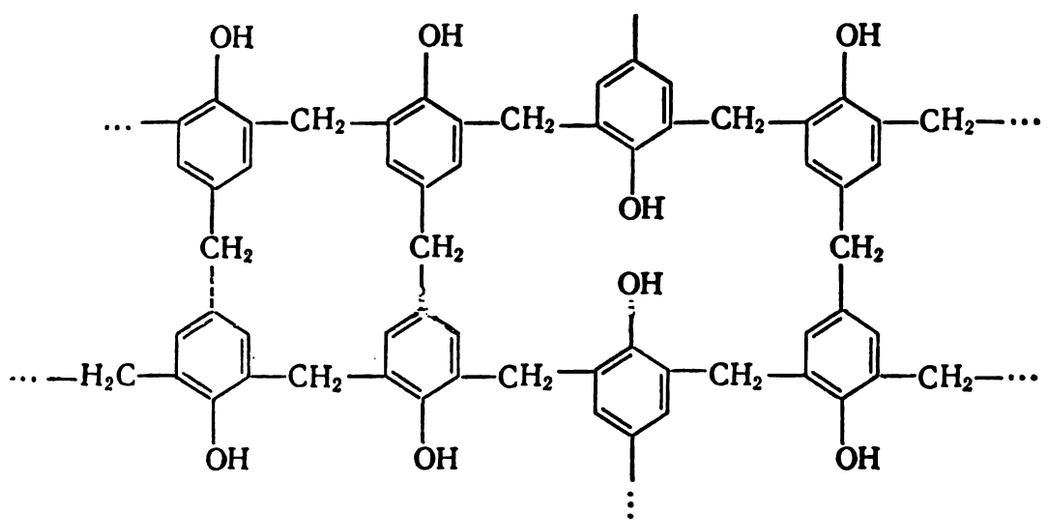
Phenol and formaldehyde are polycondensed when the components are heated for a long time in the presence of acid or base catalysts. At first, a clear yellowish liquid, which contains the methylol derivatives of phenol, is formed (see Sec. 10.9).

These products condense with one another as they are heated further, at first forming a slightly branched polymer of the following type:



The molecular mass grows gradually. If polycondensation is stopped when the molecular mass is 700-1000, *resol*, a solid, very brittle transparent mass similar to amber, is obtained. This material readily dissolves in organic solvents (alcohol, acetone).

Such solutions are used as lacquers. Resol melts at 60-90°C, and it is used for making *moulding powders*. To this end, the resin is mixed with a filler (wood meal, kaolin, ground mica, quartz, graphite, and fibrous materials, including glass fibre), dyes and other additives. Diverse articles are made out of this mixture in a hot mould. Immediately after moulding, these articles acquire a beautiful smooth surface (it does not need to be additionally coloured, polished, etc.), and they are very strong, both mechanically and chemically. In moulding, the resol resin is polycondensed further with the formation of a three-dimensional polymer called *resite*:



Resite neither melts nor dissolves.

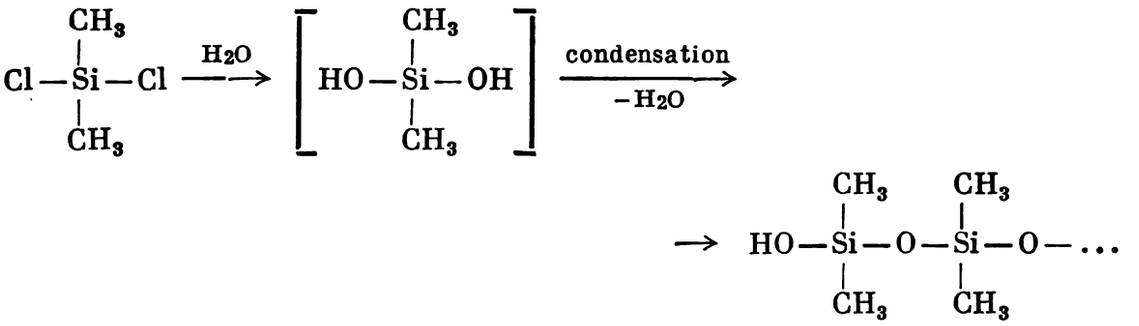
Thus, resol is a *thermosetting* polymer, i.e., it irreversibly changes its structure and properties on heating.

Materials obtained from phenol-formaldehyde polymers are known in the technological field by different names, depending on the type of filler. Light, porous materials called *plastic foams* can also be obtained from resins.

The products of polycondensation of phenol and its analogues with other aldehydes or α-oxides, and the products of polycondensation of aldehydes with aniline, urea and other nitrogen-containing compounds, are also built in the above-mentioned way.

23.10. Organosilicon Polymers. High-molecular-weight substances which, besides organic radicals, have silicon in their composition, are of great importance in technological processes. Academician K. A. Andrianov made the greatest contribution to the elaboration of this field of chemistry of high-molecular-weight compounds.

Organosilicon polymers whose chains are composed of the atoms of silicon and oxygen, i.e., *polysiloxanes* (silicones), are now most commonly used. They are obtained by hydrolyzing dialkyldichlorosilanes:



The initial hydrolysis products, silanediols, are condensed with the elimination of water, and they turn into polymeric siloxanes.

Methyl siloxane rubber, whose especially valuable property is thermal stability, is obtained by the foregoing scheme. Organosilicon-based rubber is elastic in the temperature range from —60°C to +250°C. It is a good electrical insulator, and is highly resistant to the action of chemical reagents. Liquid polysiloxanes are used as heat-resistant lubricants. Cloth, paper or wood is made water-proof by impregnating it with polysiloxanes.

Valuable properties are possessed by polymers which, besides silicon, have aluminium, titanium, boron and other elements in their molecules.

* * *

Synthetic materials are now being produced in a great variety. They are used in the most diverse fields: they substitute important

metallic parts in planes, rockets and motor-cars, and are employed as construction materials in machine-building and as insulators in the electrical-engineering industry; moreover, they are used for obtaining textiles and consumer goods, structuring the soil, and making various tubes and films, and they replace ceramic articles (bath-tubs and tiles) in construction.

Ion-exchange resins (ion exchangers) are now very important. They are high-molecular-weight substances which contain ionogenic groups (SO_3H, COOH, NH_2, etc.). Ion exchangers are used to extract valuable components from sea water, purify sewage, desalinize water, and remove inorganic ions from sugar syrups and medicinal solutions. They are also used for separating complex electrolytic mixtures (ion-exchange chromatography), and serve as catalysts for esterification, hydration, etc. Moreover, polymers are employed as *adsorbents* for separating organic substances.

Chapter 24

METHODS OF INVESTIGATING ORGANIC SUBSTANCES

24.1. Determination of the Structure. In reading the works by the classics of organic chemistry, one inevitably notices how carefully they describe the organic substances which they obtained and how much attention they devote to the purification and characterization of these substances. In modern publications, this stage of an organic chemist's work appears to be far more laconic: an empirical formula and the melting or boiling point are given, followed by different modern characteristics which are obtained by physico-chemical methods of investigation, i.e., the data of optical spectra, nuclear magnetic resonance, mass spectrometry, etc. Such a description often creates the false impression on the beginning organic chemist that the modern methods of investigation do not require of him to carefully purify a substance, and that these methods can "themselves" give a correct answer. This is a very dangerous delusion. A correct analysis can be made, and a precise melting point, a correct spectral or other characteristic can be given, only when work is done with an ideally pure substance. The data of an investigation involving a contaminated substance can give rise to serious errors. Therefore, the problem of purifying substances is, as formerly, very important.

We have become acquainted with the methods of purifying organic substances in Sec. 1.2. A pure organic substance is analyzed qualitatively and quantitatively, and the summary (empirical) formula is determined. But this is only the beginning of its investigation. The next stage is the establishment of its *structural formula.* Various physico-chemical methods (see further) are of great help to the modern researcher in this respect. However, the problem of establishing the structure can be solved by purely chemical means as well. Let us illustrate this by taking the example of a substance for which the empirical formula $C_4H_6O_2$ was established.

The test substance consists of crystals which melt at 71°C and somewhat dissolve in water; moreover, the aqueous solution shows an acid reaction. The last property gives the idea that it is carboxylic acid. The assumption that the carboxyl group is present can be confirmed by obtaining several functional derivatives: salts, esters, acid chloride, and amide. After becoming convinced that the substance

has the carboxyl group, we can specify the formula by writing it as C_3H_5—COOH.

The radical C_3H_5 is short of two hydrogen atoms for complete saturation; therefore it should contain a double bond or a cycle. After carrying out reactions for the double bond (the decolorization of bromine water or the alkaline solution of potassium permanganate) and having become convinced that the substance is unsaturated, we obtain three structural formulas to which the test substance can correspond:

$$\underset{\text{I}}{CH_3-CH=CH-COOH} \qquad \underset{\text{II}}{CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COOH} \qquad \underset{\text{III}}{CH_2=CH-CH_2-COOH}$$

To make the right choice between these structures, the products of destructive oxidation must be studied. After ascertaining that acetic and oxalic acids are present in them, formula I can be considered proven:

$$CH_3-CH=CH-COOH \xrightarrow{[O]} CH_3-COOH+HOOC-COOH$$

Conclusive chemical evidence of the structure of an organic substance is its synthesis. In this case, such synthesis can be effected by carefully oxidizing crotonaldehyde:

$$CH_3-CH=CH-CHO \xrightarrow{[O]} CH_3-CH=CH-COOH$$

Thus, the substance of the $C_4H_6O_2$ composition in the foregoing example is crotonic acid.

The nature of functional groups which are in the test substance is ascertained chemically in most cases. Multiple bonds are detected by the reactions with bromine and potassium permanganate. Alcohols are converted under the action of chloride of dinitrobenzoic acid into the corresponding esters or under the action of phenylisocyanate into phenylurethanes. Aldehydes and ketones are detected by the formation of oximes and phenylhydrazones, and acids are detected by the formation of amides and other derivatives; acetyl or benzoyl derivatives are obtained from amines, etc. All these and many other derivatives are crystalline substances with definite melting points. They are valuable, because they make it possible not only to detect a functional group, but also identify a specific substance. This is done by comparing, in special tables, the melting points of the corresponding derivatives with those found experimentally.

For instance, if it is concluded that the above-mentioned substance of the $C_4H_6O_2$ composition is an acid, the investigation can be carried on further by subjecting the substance to the action of thionyl chloride (for obtaining acid chloride) and then aniline. After determining the melting point of the anilide obtained (m.p. 118°C), it can be ascertained from tables that anilide of crotonic acid has such a melting

point. Thus, the problem of identifying a test substance of the $C_4H_6O_2$ composition can be solved without additionally studying the nature of the radical, i.e., by simply ascertaining the nature of the functional group and obtaining a crystal derivative (anilide). The accuracy of such an identification wholly depends on the ability to separate the derivative in pure form. For instance, if anilide is purified not well enough and it is ascertained that the substance obtained has a melting point of 104°C, the acid under consideration can be mistaken for acrylic acid.

24.2. Physical Methods of Determining the Structure. Refractivity, or the determination of refractive indices by optical devices called refractometers, is one of the oldest methods of physically investigating organic compounds. Since this method is simple and precise, it is widely used for identifying liquid organic substances and estimating their purity.

Purity is estimated by comparing the refractive index found with the constant for a pure substance that is given in tables. A substance can be considered to be pure if its refractive index differs from that in literature by not more than a unit in the third decimal place (0.001).

When a substance is being identified, *molecular refractivity* (Lorentz-Lorenz equation) is calculated from both the refractive indices which have been measured and the density of a substance:

$$MR = \frac{M}{d} \times \frac{n^2 - 1}{n^2 + 2}.$$

The molecular refractivity of an organic substance is an additive quantity, i.e., it can be calculated by the structural formula of a substance as the *sum of atomic refractions* and *increments* of multiple bonds.

The values of the atomic refractivity of some elements and increments of multiple bonds calculated by Eisenlohr are given below (for the D line of sodium, it is 589 nm*):

	Atomic refraction		Atomic refraction
Carbon	2.418	Bromine	8.865
Hydrogen . .	1.100	Iodine	13.900
Oxygen		Nitrogen (in primary aliphatic	
in the hydroxyl	1.525	amines)	2.322
ethereal	1.643	Increments	
carbonyl	2.211	C=C	1.733
Chlorine	5.967	C≡C	2.389

* The abbreviation nm stands for nanometer, which is equal to 10^{-7} cm. It is used in accordance with the International System of Units, which has now been introduced instead of the old notation mμ for millimicron.

The structure of a substance is confirmed when molecular refractivity thus calculated coincides with that found from experimental data.

Suppose that the refractive index (n_D^{20} 1.4262) and relative density (d_4^{20} 0.7785) of a liquid having the molecular formula C_6H_{12} (molecular mass: 84.16) were measured. The data obtained were used to find molecular refractivity by the Lorentz-Lorenz equation; it turned out to be 27.71. A compound of the C_6H_{12} composition is either cyclohexane or hexene; theoretical molecular refractivity as the sum of atomic refractivity and increments of multiple bonds can be calculated for both substances:

	Cyclohexane	Hexene
C_6	6×2.418	6×2.418
H_{12} . . .	12×1.100	12×1.100
Double bond	—	1×1.733
	27.71	29.44

Molecular refractivity found experimentally coincides with that calculated for cyclohexane. Thus, the substance is cyclohexane.

The presence of conjugated double bonds in the molecule of a substance increases molecular refractivity which is found experimentally in comparison with that which is calculated. This phenomenon, called *exaltation of molecular refractivity*, is used for detecting conjugated double bonds.

Spectroscopy. Methods based on *absorption spectra* are especially important physical methods of investigating organic compounds. What they all have in common is that light (or, to be more exact, any electromagnetic radiation, see further) may be absorbed when it passes through a substance. Physically, absorption consists in the partial transformation of light energy into the internal energy of a substance, i.e., the energy of its molecules, atoms, electrons, and nuclei.

Absorption obeys quantum laws: it is not any light which is absorbed, but only that whose energy of quanta (photons) corresponds to the differences in the energies of two states of a molecule, i.e., the ground state and the excited state, which is created when the relevant quantum is absorbed. This is expressed mathematically in the condition formulated by Bohr:

$$E' - E_0 = h\nu$$

where E' = energy of the excited state;
E = energy of the ground state;
h = Planck's constant;
ν = radiation frequency (when frequency is being measured in "inverse centimetres", cm^{-1}, it is equal to $1/\lambda$, i.e., it is an inverse quantity of the wavelength).

If "white" light (i.e., radiation which contains light quanta of the most diverse size, or, in other words, rays of different wavelengths) passes through a substance, only the part of it that satisfies the foregoing conditions is absorbed. The other part passes through the substance without weakening and, after passing through, assumes a colour which *supplements* that of absorbed light. For instance, potassium permanganate intensively absorbs quanta of the dark blue-green part of the spectrum (480-560 nm); as a result, light which has passed through is violet, i.e., the well known colour of permanganate solutions. The dependence of absorption on the wavelength, called the *absorption spectrum* of permanganate, is given in Fig. 24.1.

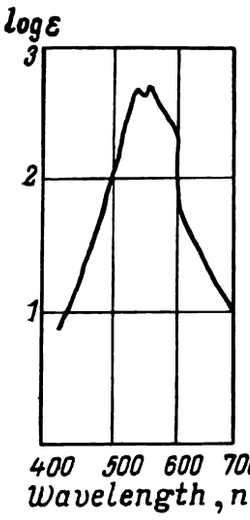
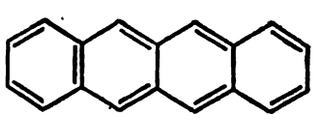


Fig. 24.1. Permanganate absorption spectrum

Absorption can be observed not only in the visible region (like for permanganate), but also in the invisible parts: the ultraviolet and infrared parts.

To understand the link between the nature of absorption and the structure of an organic substance, let us return to Bohr's condition $E' - E_0 = h\nu$. The closer are both energy levels to one another, the less is the expenditure of energy on excitation and the less is the energy that can be possessed by a light quantum, i.e., the less is the frequency ν (and, conversely, the greater is the wavelength that corresponds to it). The difference in energies $E' - E_0$ is ultimately determined by electron *mobility*. For instance, the electrons of the σ-bonds are linked very firmly, and quanta having great energy are needed for exciting them. Therefore, saturated hydrocarbons, alcohols and ethers absorb only in the very remote ultraviolet region. Ethylene, which has mobile π-electrons, absorbs at 193 nm. Conjugated double bonds in butadiene, $CH_2=CH-CH=CH_2$, which has even greater mobility of π-electrons, absorbs at 217 nm. In benzene, the π-electron system has several absorption bands, and the bands of the longest wavelength are in the 260-270 nm range. Naphthalene absorbs at 314 nm, while anthracene, at 380 nm. These examples show that absorption gradually shifts toward the long-wave region as conjugation grows (i.e., as electron mobility grows). But all the above-mentioned compounds are *colourless*, because their selective absorption is in the ultraviolet region of spectrum. Visible yellow colour appears only for naphthacene ($\lambda_{max} = 480$ nm):



Thus, selective absorption in the *visible region of spectrum* and, consequently, colour are possessed by compounds having especially mobile, readily excitable electrons. They are mobile due to both the creation of conjugated systems and the inclusion of free electron pairs or unpaired electrons, which produce an anionic charge, into conjugation. The regularities which were formerly established only empirically are thus physically substantiated.

For example, benzene (Fig. 24.2) has a characteristic band with several maxima (fine structure) in the 240-260 nm range, and the

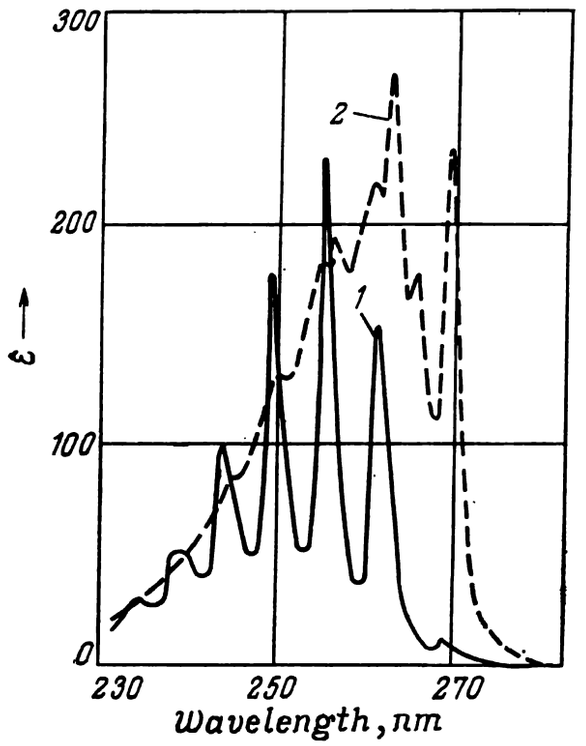


Fig. 24.2. Ultraviolet spectra of benzene (*1*) and toluene (*2*)

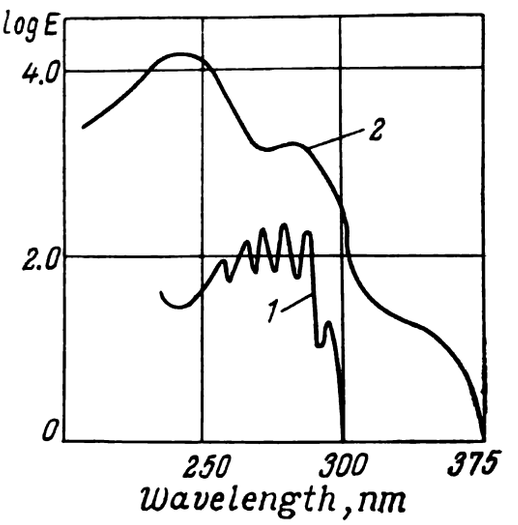


Fig. 24.3. Ultraviolet spectra of benzene (*1*) and benzaldehyde (*2*)

introduction of alkyl groups or other substituents, which have no multiple bonds or free electron pairs, does not change the nature of the spectrum, but merely slightly shifts absorption toward longer wavelengths. If the benzene ring becomes conjugated with multiple bonds or free electron pairs of a substituent, the nature of the spectrum changes, as can be seen from the absorption spectrum of benzaldehyde (Fig. 24.3). In this case, the fine structure disappears and absorption increases 100 times (in Fig. 24.3, the vertical scale is logarithmic!)

Thus, *ultraviolet spectra* (the wavelength is in the 200-400 nm range) give valuable information on the structure of organic molecules. Absorption in this region is connected with the excitation of valence

electrons, and therefore ultraviolet spectra reflect especially well the structure of systems with mobile electrons, particularly aromatic compounds.

Photons of long-wave radiation (infrared rays) carry relatively low energy, which can stimulate the vibration of atoms in molecules. But the energy of vibration of atoms depends on their own nature and the nature of a bond in the molecule (i.e., on the atoms and the way the bond is effected). Therefore, *infrared absorption spectra* (the wavelength is in the 1-10μ range, i.e., the frequency of waves is of

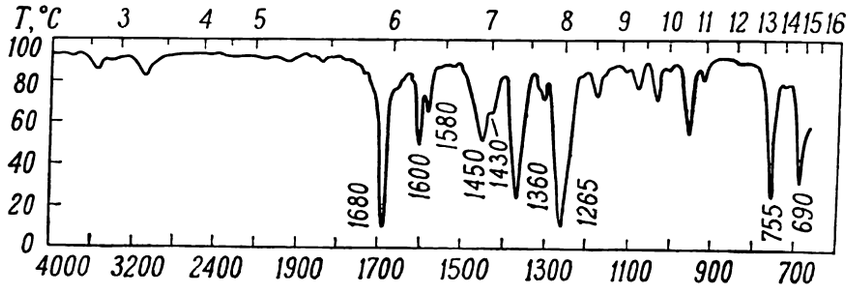


Fig. 24.4. Infrared spectrum of acetophenone

the order of 500-5000 cm^{-1}) give especially valuable information on the structure of molecules of organic compounds. The infrared spectrum of acetophenone, $C_6H_5—CO—CH_3$, is given as an example in Fig. 24.4.

The band 1680 cm^{-1} is engendered by vibrations of the carbonyl group; this characteristic band exists near 1700 cm^{-1} for all carbonyl compounds. The bands 1600, 1580, 1450, 755 and 690 cm^{-1} characterize the monosubstituted benzene ring, and the bands 1430 and 1360 cm^{-1} relate to the methyl group.

Nuclear magnetic resonance spectra are now of great importance. It should be noted without any particularities that the absorption of electromagnetic radiation of very high frequency (i.e., of longer wavelengths) is measured in this case. Nuclear magnetic resonance (NMR) involves frequencies of 0.1-0.01 cm^{-1}, i.e., the centimetre radio-wave region; therefore, the nuclear magnetic resonance method is also called *radiospectroscopy*. This method is used most frequently as *proton* magnetic resonance (PMR), which gives exact characteristics of the hydrogen atoms in the compound. The NMR spectrum of diacetone alcohol, $(CH_3)_2COH—CH_2—CO—CH_3$ (Fig. 24.5), is very simple, i.e., each type of hydrogen atoms has its own signal in the form of a single line. Such a spectrum indicates that there is no interaction between protons of different types in the compound; it occurs because all the groupings which contain hydrogen are isolated from one another, since the carbon atom and the C=O group, which have no protons, are between them.

Although ethyl alcohol is a compound of greater simplicity than diacetone alcohol, its NMR spectrum, being given in Fig. 24.6, is

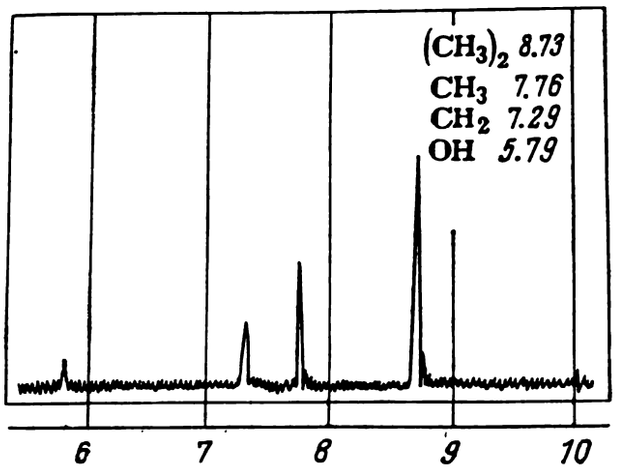


Fig. 24.5. Nuclear magnetic resonance spectrum of diacetone alcohol

more complex than that of diacetone alcohol. In ethyl alcohol, protons standing at the adjacent atoms interact with one another. As a result, instead of single lines, groups of lines originate (*line splitting occurs due to spin-spin interaction*). Additional data on molecular

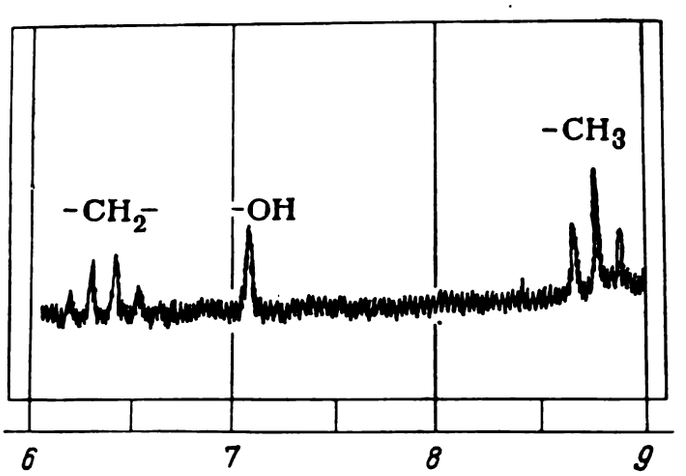


Fig. 24.6. Nuclear magnetic resonance spectrum of ethanol

structure are obtained when the nature of splitting is carefully analyzed. Thus, two types of information are contained in the nuclear magnetic resonance spectra: the *chemical shift* (signal position) and the *constants of spin-spin splitting*.

The nuclear magnetic resonance method is the most powerful tool now used for studying organic compounds. It not only gives information on the chemical and three-dimensional structure of a substance, but also often makes it possible to experimentally estimate the electronegativity of individual groups and the direction and force of mesomeric and inductive electron effects.

Spectral methods include *spectropolarimetry*, which is used for studying optically active substances, and it gives valuable information on their structure, configuration and conformation. The method

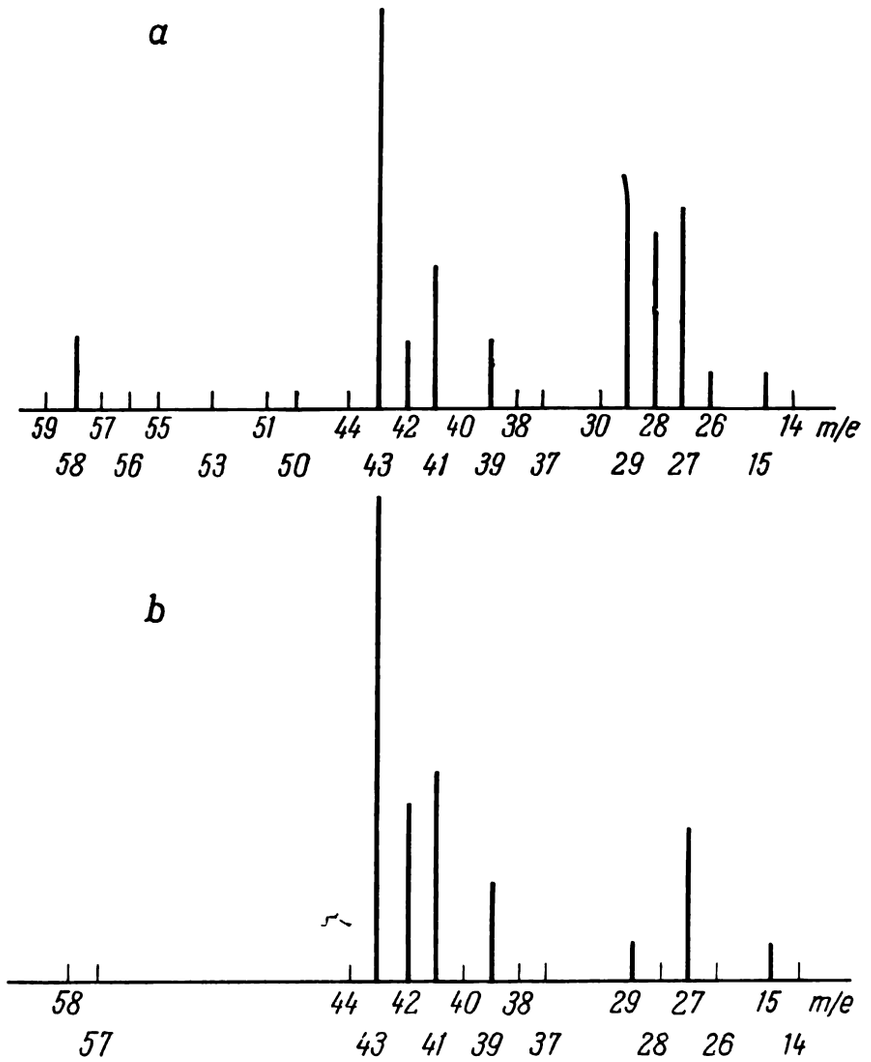


Fig. 24.7. Mass spectra of butane (*a*) and isobutane (*b*)

differs from ordinary polarimetry in that the angle of rotation is measured at different wavelengths; this gives a peculiar "rotation spectrum", which is known as the *optical rotatory dispersion curve.*

Mass spectrometry is a method of investigating organic substances, and is based on the study of "fragment ions", which are formed as a result of electron bombardment of an electron beam having an energy of several tens of electron volts. The results are obtained in the form of *mass spectra*, which register the types of "fragment ions" obtained (a characteristic of each of them is the mass-to-charge ratio, *m/e*) and the intensity of each mass spectral line, which reflects the number of ions of a given type that are formed. Mass spectrometry is used

to determine the structure of organic compounds and their molecular mass. Even slight differences in structure are reflected in mass spectra, as is evident from the mass spectra of butane and isobutane (Fig. 24.7).

Besides being used in research laboratories, mass spectrometry is employed as a control method in the petrochemical and other industries.

Electron paramagnetic resonance (EPR) is based on the absorption of electromagnetic waves by paramagnetic substances in the permanent magnetic field. Paramagnetic properties are possessed, in particular, by free radicals, and the electron paramagnetic resonance method is used in organic chemistry for detecting and studying them.

CONCLUSION

Organic chemistry has led an independent existence for about 150 years. At first, it was a science of natural substances, but later it became largely a study of synthetic compounds. As early as the nineteenth century, achievements in synthetic organic chemistry became the basis of several industries producing synthetic dyes, medicinals and explosives. In the twentieth century, petroleum has become the basis of the heavy organic synthesis industry, i.e., the high-tonnage production of pure hydrocarbons, alcohols, ketones, acids and their derivatives, which are raw material for obtaining various products. Synthetic high-molecular-weight compounds began to be put out on a large scale, and their production became of paramount importance. Clothing, footwear, most household articles, medicinals, and many other things are now being produced by organic synthesis. An important task of organic chemistry even today is to obtain new useful substances and materials.

The necessary substances are now no longer obtained accidentally, and the direction of research can be planned with certain probability. But the link between the structure and the physical, chemical and physiological properties of substances will still be an important scientific problem in organic chemistry in the immediate future. Practical and theoretical problems will be solved as the means of investigation (i.e., synthesis, analysis, and diverse physico-chemical methods) develop further.

Organic chemists have always studied natural substances. Today, this is especially important, both theoretically and practically, because organic chemistry, together with biology, has reached the stage at which the chemical principles of life can be revealed. This study creates a scientific basis for fighting the most serious diseases and increasing agricultural output.

Organic chemistry is connected with virtually all the aspects of Man's diverse activity and is a constituent of the national economy.

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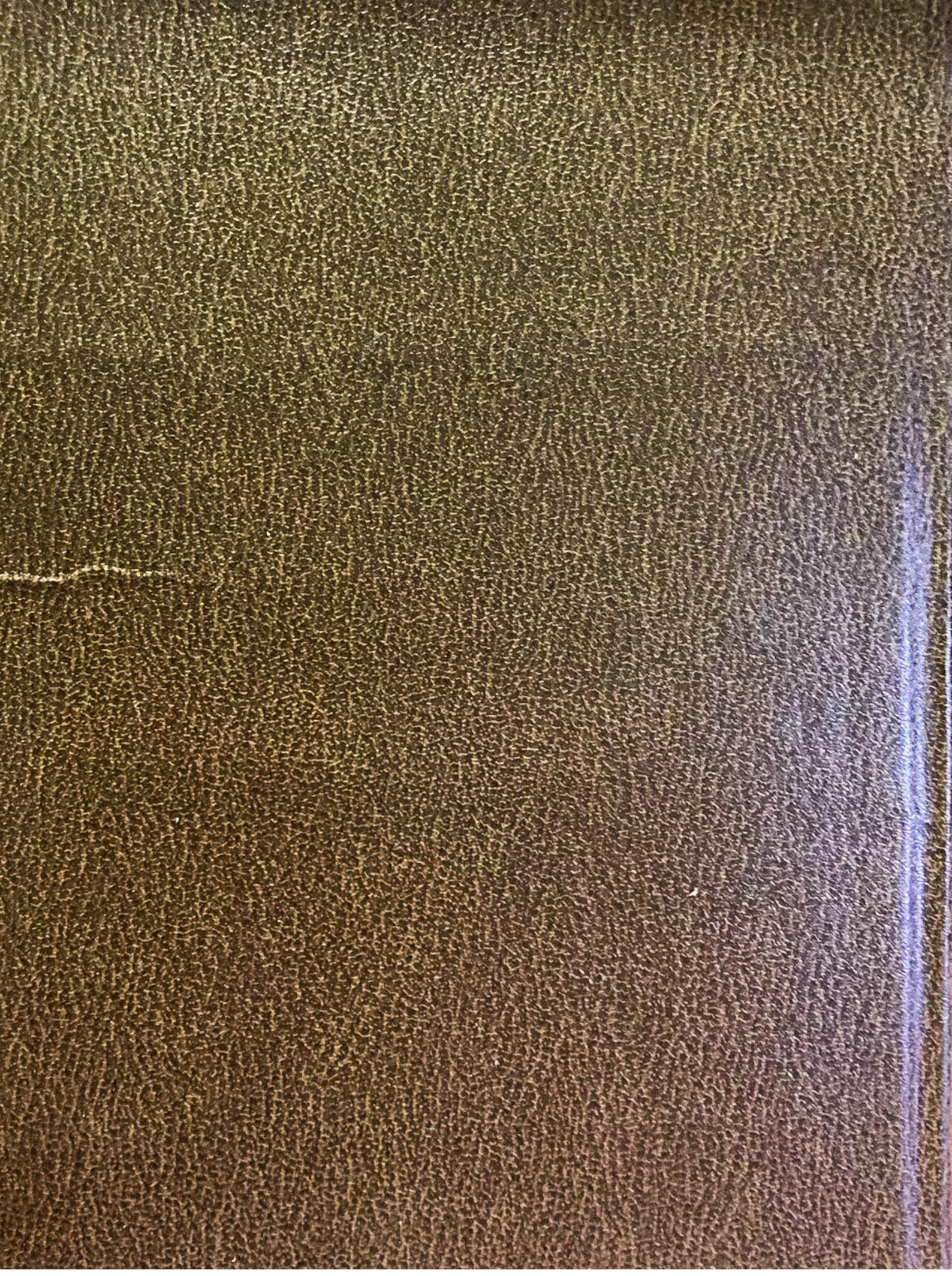

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